150. *Dioxan-induced Association of n-Alkyl Titanates.*

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Measurements of freezing-point depression are used in studying the association resulting from intermolecular Ti·OR·Ti bridges between molecules of n-alkyl titanates in dioxan.

The oxygen-donating properties of dioxan towards titanium are found to be intermediate between those of ethoxide and the remaining alkoxides, so that the association equilibria in dioxan depend on the nature of the alkyl substituent. Thus the association of titanium(IV) ethoxide is insensitive to whether benzene or dioxan is the solvent, indicating that the Ti·OEt·Ti bridges are not broken by dioxan. On the other hand, novel association behaviour is observed for the n-propyl, n-butyl, and n-pentyl alkoxides, which reveals that the intermolecular bridges have been broken, that solvation of titanium by dioxan has occurred, and in consequence that large solute aggregates are created by the bifunctional dioxan molecule bridging $[Ti(OR)_4]_x$ species in solution.

The association of alkyl titanates in solution is represented by series of successive equilibria of the general type, $(Ti)_{x-1} + (Ti) \rightleftharpoons (Ti)_x$. The equilibrium constants for each stage place the oxygen-donor strengths towards titanium as $OEt > C_4H_8O_2 > OPr^n > OBu^n > OC_5H_{11}\text{-n} > OBu^t$. It is suggested that the steric requirements of the n-alkyl group probably determine this sequence. Thus titanium(IV) t-butoxide is monomeric at all concentrations.

TITANIUM(IV) n-alkoxides form polynuclear species in the solid, the liquid, and the solution state. A recent *X*-ray structure determination [1] has revealed that crystalline titanium(IV) ethoxide is tetrameric, four TiO_6 octahedra sharing edges. The oxygen of the ethoxy-group simultaneously functions as a monodentate, bidentate, and tridentate atom with respect to titanium in the tetranuclear structure.

The polymeric nature of liquid titanium(IV) n-alkoxides is inferred from their high viscosity, boiling points, and latent heats of evaporation,[2] and from the abnormal values of Trouton's constant.[3] Studies of the apparent molecular weight of these substances by cryoscopy in benzene [4] and by ebulliometry in alkanols [5] indicate that association persists in solution. The dearth of addition products of alkyl titanates has been ascribed by Bains and Bradley [6] to co-ordinative saturation of the titanium atom by autocomplex formation.

Since the average molecular complexity *n* of $[Ti(OR)_4]_n$ in benzene is always higher for R = ethyl than for R = n-butyl at any equivalent concentration [7] it seems likely that the relative strength of intermolecular n-alkoxy-bridges depends on, *inter alia*, the length of the alkyl chain. Accordingly, the present investigation was undertaken in an attempt to differentiate between the relative strengths of n-alkoxytitanium bridges by cryoscopy in dioxan, a solvent with donor properties toward titanium of a similar magnitude to those of n-alkoxy-groups. The lower homologues, ethoxide, n-propoxide, n-butoxide, n-pentyl oxide, and t-butoxide, were selected for this study.

[1] Ibers, *Nature*, 1963, **197**, 686.

[2] Bradley, " Progress in Inorganic Chemistry," Interscience Publ., Inc., New York, 1960, Vol. II.

[3] Wardlaw, *J.*, 1955, 3569.

[4] Coughlan, Smith, Katz, Hodgson, and Crowe, *J. Amer. Chem. Soc.*, 1951, **73**, 5652; Cullinane, Chard, Price, Millward, and Langlois, *J. Appl. Chem.*, 1951, **1**, 400.

[5] Bradley, Mehrota, Swanwick, and Wardlaw, *J.*, 1953, 2025; Winter, *J. Oil Colour Chemists' Assoc.*, 1953, **36**, 689; Bradley, Gaze, and Wardlaw, *J.*, 1957, 469.

[6] Bains and Bradley, *Canad. J. Chem.*, 1962, **40**, 1350.

[7] Martin and Winter, *Nature*, 1963, **197**, 687.

EXPERIMENTAL

Tetra-n-alkyl titanates.—The ethyl, n-propyl, and n-butyl derivatives of titanium(IV) were prepared from titanium tetrachloride and the appropriate alcohol in the presence of ammonia by the method previously described.[8]

Tetra-n-pentyl titanate was prepared by refluxing tetra-n-butoxytitanium(IV) with an excess of n-pentyl alcohol for 1 hr. The excess of alcohol was then removed by distillation and the ester purified by distillation under reduced pressure (Found: Ti, 12·1. Calc. for $C_{20}H_{44}O_4Ti$: Ti, 12·1%).

Molecular weights were determined by the method previously described.[8] Dioxan was purified as recommended by Vogel.[9]

RESULTS AND DISCUSSION

The variation with concentration of the average degree of association of the alkoxides $Ti(OR)_4$, where R = Et, Bu^t, Pr^n, Bu^n, or $n-C_5H_{11}$, in dioxan solution at the freezing point (6°) is shown in Figs. 1 and 2. Three categories of behaviour can be discerned. Titanium
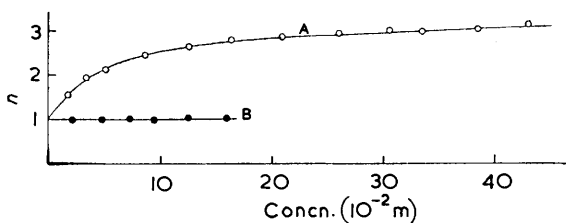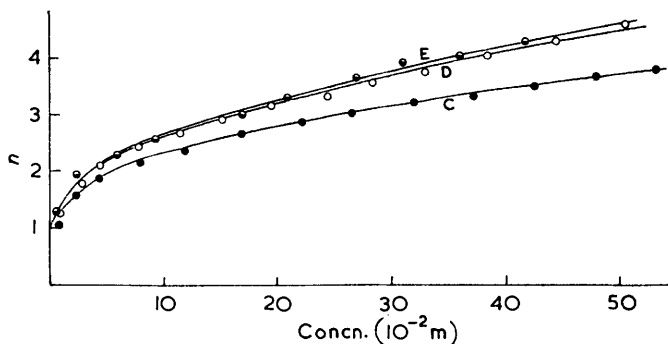

FIG. 1.

FIG. 2.

FIGS. 1 and 2. Variation of degree of polymerization (*n*) of (A) $Ti(OEt)_4$, (B) $Ti(OBu^t)_4$, (C) $Ti(OPr^n)_4$, (D) $Ti(OBu^n)$, and (E) $Ti(O\cdot C_5H_{11}-n)_4$ with concentration.

tetra-t-butoxide is monomeric at all concentrations studied; analogous behaviour of this ester is observed in benzene solution [10] and has been ascribed [3] to effective shielding of the central titanium atom by the bulky t-butyl group so that expansion of the co-ordination sphere of titanium is prevented.

Secondly, for the tetraethoxide the average molecular complexity increases from $n = 1$ at zero concentration (extrapolated) to 3·16 at the highest concentration studied $(42 \times 10^{-2}m)$, similarly to the behaviour of this compound in the non-co-ordinating solvent

[8] Martin and Winter, *J.*, 1961, 2947.
[9] Vogel, " Practical Organic Chemistry," Longmans Green and Co., London, 1956, p. 177.
[10] Martin and Winter, unpublished results.

benzene.[7]   Here again the full curve (Fig. 2) is calculated on the basis of a model which assumes that association to dimeric, trimeric, and tetrameric species occurs by successive equilibria:

$$2M_1 \rightleftharpoons M_2; \quad K_2$$
$$M_2 + M_1 \rightleftharpoons M_3; \quad K_3$$
$$M_3 + M_1 \rightleftharpoons M_4; \quad K_4$$
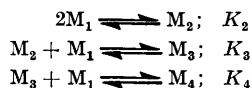
The results were fitted by a least-squares procedure in which values for K_2, K_3, and K_4 were selected by trial and error to minimize the square of the residuals.   Attempts to fit models which assumed association to species of a lower order than tetrameric were unsuccessful (see ref. 7).   This result is in harmony with Ibers's structure determination.[1] The close similarity of the association behaviour in benzene and in dioxan is apparent from the values of the equilibrium constants given in Table 1.   The major difference is the larger constant K_2.   Fig. 3 shows the relative abundance of monomeric and polymeric species in dioxan, and in Table 2 these are compared with corresponding values for benzene solution.   The population of tetramers in dioxan is very close to that in

TABLE 1.

Association equilibrium constants (kg. mole^{-1}) for Ti(OEt)$_4$ in benzene and in dioxan at 6°.

	K_2	K_3	K_4
In C$_6$H$_6$	100	110	200
In dioxan	20	88	200

TABLE 2.

Relative abundance of titanium tetraethoxide polymer species in benzene and in dioxan.

Concn. (10^{-2}m)	M$_1$ (%) Dioxan	C$_6$H$_6$	M$_2$ (%) Dioxan	C$_6$H$_6$	M$_3$ (%) Dioxan	C$_6$H$_6$	M$_4$ (%) Dioxan	C$_6$H$_6$
2	65	47	10	25	8	13	17	15
4	53	37	12	24	11	17	23	22
6	46	31	12	23	12	19	30	27
8	40	26	11	22	13	20	36	32
10	36	23	11	21	13	21	40	35
12	33	21	11	20	14	21	42	38
20	25	16	10	17	15	21	50	46

benzene.   The relative abundance of monomers is increased at the expense of dimers and trimers.   This may be ascribed to greater stability of a solvated (octahedral) monomer in dioxan compared with an unsolvated (tetrahedral) monomer in benzene.

Clearly then, the association equilibria for the polymeric species is not grossly disturbed by the presence of a solvent with donor properties much stronger than those of benzene. This indicates that the ethoxide group is the stronger donor towards titanium, so that there is no rupture of Ti·OEt·Ti bridges, with concomitant modification of the association equilibria.

The association behaviour of the remaining esters (Pr^n, Bu^n, and n-C$_5$H$_{11}$) differs from those discussed above.   At very low concentration in dioxan the monomer again is the preferred species.   As the concentration is increased, the apparent molecular weight increases as before but the average degree of polymerization continues to rise nearly linearly and there is no indication of a limiting value up to the highest concentration studied (0·5m).   The gradient of the association curves, dn/dc, decreases in the order n-C$_5$H$_{11}$ > Bu^n > Pr^n.   We believe that this provides a novel demonstration of the bifunctional nature of the dioxan molecule.   Previously this characteristic has

been invoked to explain the existence of a crystalline copper(II) formate complex, $Cu_2(H \cdot CO_2)_4, C_4H_8O_2$, which can be formulated [11] with the chain structure:

$$. . . Cu(H \cdot CO_2)_4 Cu \cdot O \cdot C_4H_8 \cdot O \cdot Cu(H \cdot CO_2)_4 Cu \cdot O \cdot C_4H_8 \cdot O . . .$$
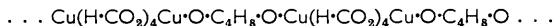
Also, it has been established [12] that dioxan can co-ordinate with titanium in titanium tetrachloride. We therefore propose that the present unusual association behaviour arises because the donor properties of dioxan are sufficiently strong to rupture the n-propoxy-, n-butoxy-, and n-pentyloxy-bridges so that co-ordination of dioxan to titanium can occur; further, that the bifunctional character of dioxan is developed in the present environment so that polymeric bridged alkyl titanates of following type $-[Ti(OR)_4 \cdot OC_4H_8O \cdot Ti(OR)_4]^-$ are formed.

The observed concentration dependence of the average degree of association can be accurately fitted by employing this model (see Fig. 3; the full lines represent theoretical
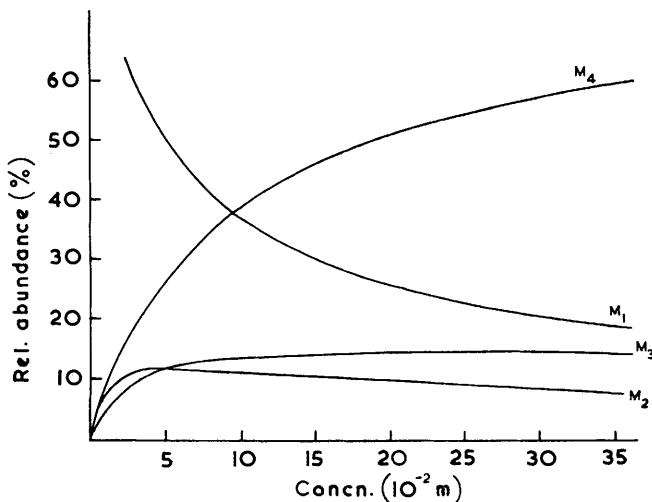

FIG. 3. Relative abundances of the species, M_1 to M_4, for $Ti(OEt)_4$ in dioxan, calculated for $K_4 = 200$, $K_3 = 20$, and $K_2 = 88$.

curves which have been calculated by substituting in equation 1 the estimated values for K_2 and K_i given in Table 3). We continue to assume an equilibrium constant K_2 for the dimer formation, but now represent the successive production of i-mers by a series of stepwise equilibria with appropriate equilibrium constants K_i:

$$M'_{i-1} + M'_1 \rightleftharpoons M'_i; \quad K_i$$

where M'_1 represent the basic complex unit $Ti(OR)_4, C_4H_8O_2$.

The observed average degree of association is defined by:

$$n = \frac{\text{(Stoicheiometric molality)}}{\text{(No. of moles of separate solute entities per kg. of solvent)}}$$

$$= \sum_i i[M'_i] / \sum_i [M'_i]$$

$$= [M'_0] / \sum_i [M'_i]$$

$$= [M'_0] / ([M'_1] + K_2[M'_1]^2 \{1 + K_i[M'_1]^2 + (K_i[M'_1])^2 \ldots\}),$$

[11] Martin and Waterman, *J.*, 1959, 2960.
[12] Hamilton, McBeth, Beckebrede, and Sisler, *J. Amer. Chem. Soc.*, 1953, **73**, 2881.

where $[M'_0]$ represents the analytical concentration of titanium in solution in gram-atom per kg. of dioxan. Provided $K_i[M'_1] < 1$, the term in braces ($\{\}$) in the denominator will be a convergent infinite series whose sum equals, $\{1 - K_i[M'_1]\}^{-1}$. Stokes and Pugh [13] have shown that this reduces to the relation:

$$\frac{\frac{2[M'_0]}{n} - [M'_0]}{\sqrt{\{[M'_0] - [M'_0]/n\}}} = \frac{1}{\sqrt{K_2}} - \frac{[M'_0]}{n} \cdot \frac{K_i}{\sqrt{K_2}}. \tag{1}$$

Thus, a graph of $[M'_0]/n$ against the expression on the left of equation (1) should give a straight line with slope $-K_i/\sqrt{K_2}$ and intercept at $1/\sqrt{K_2}$. The present results for the propyl, butyl, and pentyl derivatives do, in fact, give straight lines. The slopes and intercepts were determined by a least-squares refinement and the values for K_2 and K_i so obtained are given in Table 3. The values are subject to appreciable error: 95%

TABLE 3.

Association equilibrium constants K_2 and K_i (kg. mole^{-1}) at 6°.

Ester	Pr^n	Bu^n	$n\text{-}C_5H_{11}$
K_2	80	121	127
K_i	32	52	55

confidence limits for K_i are about $\pm 10\%$ of the quoted values and for K_2 are about $\pm 15\%$.

It should be noted that, although the derivation of equation (1) assumes that i may tend towards infinity, the experimental values for $[M'_0]$ and n cause the series to converge rapidly and the concentration of species with $i > 20$ is negligible from an experimental viewpoint.

The values for K_2 and K_i derived from this model reveal that the equilibrium constants increase in a regular manner from n-propoxide to n-pentyl oxide. We interpret the increase in K_i as indicating progressive weakening of the Ti·OR·Ti bridge with increase in chain length, resulting in a greater ease of replacement by dioxan bridges. Accordingly, solvation accompanied by polymerization decreases in the sequence n-$C_5H_{11}O$ > Bu^nO > Pr^nO. The simultaneous increase of K_2 seems, at first, surprising. However, accommodation of dioxan by a monomeric titanium species (solvation) is likely to become progressively more difficult as the chain length increases, resulting in a displacement of the equilibrium towards the dimer.

It will be apparent that the present observations may be described equally by a more complicated model. For example, there could be dioxan bridging, not only between monomers, but also between dimers and trimers. Thus we have verified that our cryoscopic data can be fitted by equilibria involving dimeric titanium alkoxide units linked by dioxan. However, the simple model illustrates polymerization based on dioxan bridges.

Finally, we draw attention to the subtle role played by dioxan in differentiating the relative strengths of the intermolecular alkoxy-bridging in alkyl titanates. With titanium as a reference acceptor the following order of donor properties may reasonably be assumed: EtO > Pr^nO > Bu^nO > n-$C_5H_{11}O$ > Bu^tO.

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[13] Stokes and Pugh, *Austral. J. Chem.*, 1963, **16**, 211.