out from the oxygen atoms and lead to a molecule that is approximately cylindrical in shape. All intermolecular contacts are normal.

The structure depicted in Fig. 1 has several satisfying features, most prominent of which are the octahedral co-ordination of the titanium atoms and the readily visualized termination of polymerization. The relation of this structure to those of the titanium (IV) alkoxide species present in solution is as yet unknown. The structure is sufficiently different from any proposed for the trimeric species so that, at the least, reconsideration not only of the features of those structures but also of the proposed mechanisms of hydrolysis seems necessary. What is more important, however, is a re-examination of the evidence in favour of the trimeric species as the largest present. To this end Martin and Winter, as reported in the following communication, have carried out extensive cryoscopic molecular weight studies on titanium (IV) ethoxide and butoxide in benzene. They indeed find evidence for a tetrameric titanium (IV) ethoxide species in benzene solutions.

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JAMES A. IBERS

Chemistry Department,
Brookhaven National Laboratory,
Upton, Long Island, New York.

[1] Bradley, D. C., Gaze, R., and Wardlaw, W., *J. Chem. Soc.*, 3977 (1955).
[2] Martin, R. L., and Winter, G., *Nature*, **188**, 4747 (1960).
[3] Bradley, D. C., and Westlake, A. H., *Nature*, **191**, 273 (1961).
[4] Martin, R. L., and Winter, G., *Nature*, **191**, 274 (1961).
[5] Martin, R. L., and Winter, G., *J. Chem. Soc.*, 2947 (1961).
[6] Caughlan, C. N., Smith, H. S., Katz, W., Hodgson, W., and Crowe, R. W., *J. Amer. Chem. Soc.*, **73**, 5652 (1951).
[7] Bradley, D. C., Gaze, R., and Wardlaw, W., *J. Chem. Soc.*, 721 (1955).
[8] Crowe, R. W., and Caughlan, C. N., *J. Amer. Chem. Soc.*, **72**, 1694 (1950).

Association of Titanium (IV) Alkoxides in Benzene

THE single crystal X-ray structure determination of titanium (IV) ethoxide described in the preceding communication establishes the fact that the molecule is a tetramer formed by the stacking of four TiO_6-octahedra so that edges are shared (Fig. 1). Dr. Ibers's analysis also confirms the long-accepted belief that intermolecular attachment between $Ti(OC_2H_5)_4$ molecules is through ethoxide bridges (two per titanium atom) and reveals that two types of intramolecular ethoxide bridges can be discerned in the molecular unit.

While it is not unknown for a structural entity in the solid state to differ from that present in solution, it now becomes important to extend previous cryoscopic measurements in benzene[1,2] to higher concentrations to establish whether the degree of association of titanium (IV) *n*-alkoxides can, in fact, exceed three.

For titanium (IV) *n*-butoxide we have now increased the range of concentration over which molecular weight measurements have been made from $15{\cdot}1 \times 10^{-2}$ to $34{\cdot}0 \times 10^{-2}$ molal, that is, approximately 11·5 wt. per cent (Fig. 2). The degree of association of the butoxide at the highest concentration is 2·6. We have also recently completed studies of the concentration dependence of the degree of association of titanium (IV) ethoxide in benzene using the techniques described elsewhere[2]. The data are presented graphically in Fig. 2 and it will be seen that although the curve rises more steeply than for the *n*-butoxide, even at the highest concentration the experimental degree of association has not exceeded three. Activity effects and problems associated with supercooling intervene in more concentrated solutions so that it cannot be resolved whether average degrees of association greater than three occur.

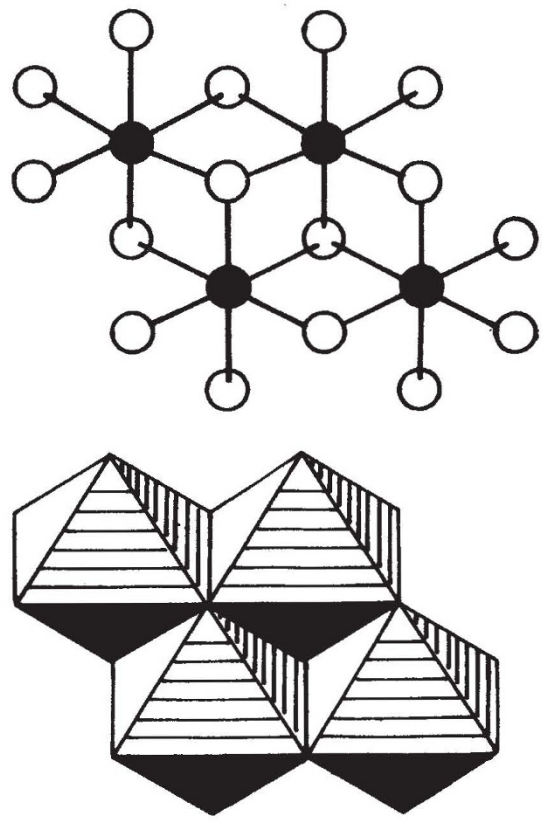

Fig. 1. Molecular structure of $Ti_4(OC_2H_5)_{16}$ showing two types of ethoxide bridging groups and the stacking of the TiO_6-octahedra

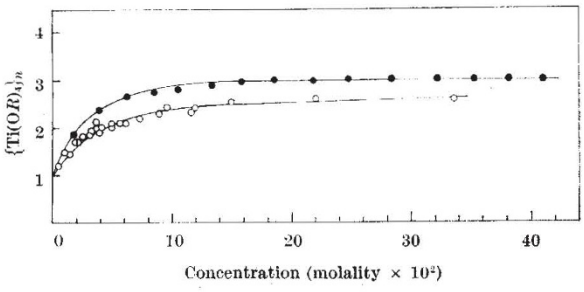

Fig. 2. Degree of association, *n*, of titanium (IV) *n*-alkoxides in benzene. ●, $R = C_2H_5$; ○, $R = n$, C_4H_9

It is significant, however, that while the new data for the butoxide can still be described by the curve previously derived[2] for an equilibrium involving monomeric, dimeric, and trimeric species in benzene, such a description is no longer adequate for the ethoxide. The introduction of at least one further equilibrium species, namely a tetramer, is required to fit the experimental variation of the average degree of association with concentration. Since the experimental values for the butoxide can also be fitted in terms of a similar set of equilibria, it is not possible to resolve cryoscopically whether for this compound also the limiting degree of association is greater than three.

Cryoscopic studies in solvents other than benzene are being made.

R. L. MARTIN
G. WINTER

Department of Inorganic Chemistry,
University of Melbourne.

[1] Caughlan, C. N., Smith, H. S., Katz, W., Hodgson, W., and Crowe, R. W., *J. Amer. Chem. Soc.*, **73**, 5652 (1951).
[2] Martin, R. L., and Winter, G., *J. Chem. Soc.*, 2947 (1961).