The Crystal and Molecular Structure of the First Hydrolysis Product ($Ti_7O_{24}Et_{19}$) of Titanium Tetraethoxide

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THE hydrolysis of titanium tetraethoxide was studied by Bradley, Gaze, and Wardlaw,[1] and as a result of their analytical and cryoscopic molecular weight studies, and the suggested trimeric structure for titanium tetraethoxide,[2] they suggested the formula $Ti_6O_4(OEt)_{16}$. It has since been shown by crystal structure studies that titanium tetraethoxide and titanium monomethoxide triethoxide are tetrameric in the solid state.[3] We have determined the structure of the first hydrolysis product of titanium tetraethoxide by *X*-ray diffraction, and find it to be $Ti_7O_{24}Et_{19}$, although the exact number of carbon atoms is still somewhat in doubt.

Crystals of this compound were grown by dissolving titanium tetraethoxide in dry ethanol and passing through this solution a slow stream of partially dried air. One of the crystals formed was selected for *X*-ray study, with the following results: Monoclinic, $a = 27{\cdot}99$, $b = 22{\cdot}42$, $c = 23{\cdot}21$ Å, $\beta = 117{\cdot}3°$, $D_m = 1{\cdot}305$, D_c (for 8 $Ti_7O_{24}C_{38}H_{95}$) = $1{\cdot}304$, space group $P2_1/a$ (No. 14). The intensities of 900 reflections, obtained with a diffractometer, using Mo-K_α radiation, were used in a structure

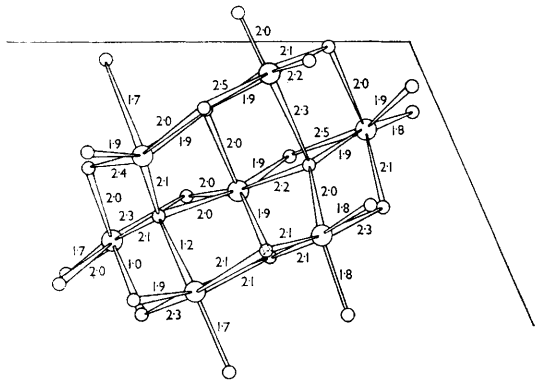

FIGURE. *The structure of* $Ti_7O_{24}Et_{19}$. *The carbons are not shown; large circles are titanium, small circles oxygen.*

analysis, which has now been refined to $R = 13\%$. Analysis of the remaining crystals gave Ti, 27·25; C, 34·7; H, 7·2%, which corresponds approximately to $Ti_7O_6(OEt)_{18}$, whereas the results of Bradley *et al.*, suggest $Ti_7O_5(OEt)_{19}$, assuming the crystallographic molecular weight.

The structure found, without C-atoms, is shown in the Figure. The Ti atoms are octahedrally co-ordinated, the TiO_6 octahedra sharing edges. The central octahedron shares six of its twelve edges with other Ti octahedra to form Ti_7O_{24}, which is shown in the figure. The Ti–O distances shown have standard deviations of about 0·1—0·3 Å.

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