Selective Inclusion of Ethanol by Triphenylsilanol. Crystal Structure and Thermal Analysis

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Triphenylsilanol is a selective host for ethanol in the presence of other simple homologous alcohols and forms a 4 : 1 coordinatoclathrate stabilised by hydrogen bonds; thermal decomposition takes place in a two-step process with the formation of a new intermediate phase.

Ethanol obtained by the fermentation of biomass is an important source of energy. However, its isolation from dilute aqueous solution is usually carried out by distillation, which is a costly process. This has led us to seek suitable host compounds which will entrap ethanol selectively, and thus to use the process of enclathration for its isolation. Several bulky organic compounds form host–guest complexes with small aliphatic alcohols as guests.[1] Some of these host molecules contain the hydroxy moiety,[1] or are carboxylic acids[2] or amides,[3] and thus form coordinatoclathrates[4] in that the host and guest molecules are linked by hydrogen bonds.

Triphenylsilanol forms an inclusion compound with ethanol and its selectivity was verified by dissolving this host in equimolar mixtures of MeOH and EtOH, PrOH and EtOH, and ethanolic solutions containing up to 40% w/w of water.

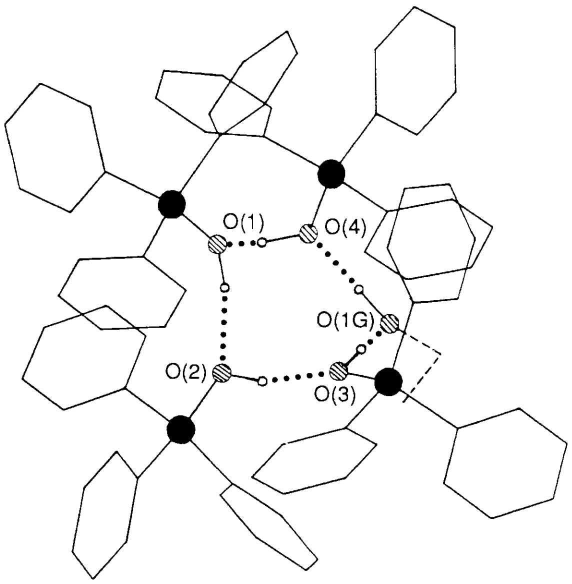

Fig. 1 Perspective view of hydrogen bonding of four host and one guest molecules. Silicon atoms are shown as filled circles and oxygens by shaded circles. The idealised guest molecule is shown by long dashed lines and the hydrogen bonds by shorter dashed lines. The H atom of EtOH was fixed in an assumed position.

The crystalline product was invariably the molecular complex with a host to guest ratio of 4 : 1.

The non-porous α-phase of triphenylsilanol crystallises in the space group $P\bar{1}$[5] with 16 molecules in the unit cell. The asymmetric unit contains two tetrameric clusters in which the four oxygen atoms lie at the apices of a tetrahedron while the phenyl rings point outwards. The hydroxy hydrogens were not located but hydrogen bonding was inferred from the short O · · · · O distances which ranged from 2.65 to 2.68 Å, as well as the broadening of the hydroxy stretching band at 3250 cm^{-1} in the IR spectrum.

The β-phase coordinatoclathrate of triphenylsilanol with ethanol† results from the opening of the host tetrahedral clusters to accommodate the guest hydroxy moiety in the hydrogen bonding scheme. This is shown in Fig. 1 which shows four host molecules and the guest ethanol in a cyclic network of the hydrogen bonds. The O · · · · O distances in this structure vary from 2.60 to 2.79 Å. The OH stretch in the IR spectrum of this compound is broad and centred at 3200 cm^{-1}. This compound has certain structural features in common with the related clathrate $Ph_3COH{\cdot}MeOH$ (1 : 1),[6] in which two

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† *Crystal data* for **1**: ·EtOH (4 : 1) $(C_{18}H_{16}OSi)_4{\cdot}C_2H_6O$, M = 1151.71, triclinic, space group $P\bar{1}$, a = 13.682(4), b = 15.119(6), c = 15.990(6) Å, $\alpha = 88.23(3)$, $\beta = 81.83(3)$, $\gamma = 87.07(3)°$, $Z = 2$, $D_c = 1.17$, $D_m = 1.16$ g cm^{-3}, crystal size = 0.25 × 0.28 × 0.41 mm.

Intensity data were measured at room temperature on a Enraf–Nonius CAD4 diffractometer using Mo-Kα (λ = 0.7107 Å) radiation to θ_{max} = 20°; 4095 unique reflections were collected. The least squares refinement converged to a final $R = 0.103$ for 3957 reflections with $I > 2\sigma(I)$; R_w = (0.112 with w $(\sigma^2F + 0.05F^2)^{-1}$. Residual electron density (max,min) = 0.93,−0.46 e $Å^{-3}$. All the host hydroxy hydrogens were located unambiguously in a difference electron density map and refined with constrained bond lengths. The phenyl rings of the host were refined as regular hexagons.

With the host atom positions satisfactorily refined, the ensuing difference electron density map yielded position of the ethanol oxygen unambiguously, but the ethanol carbons were poorly defined. The final model therefore incorporated bond length constraints on the ethanol carbons, the guest hydrogens were omitted with the exception of the hydroxy hydrogen which was fixed at 1.01 Å from the ethanol oxygen, in a linear H-bond.

Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

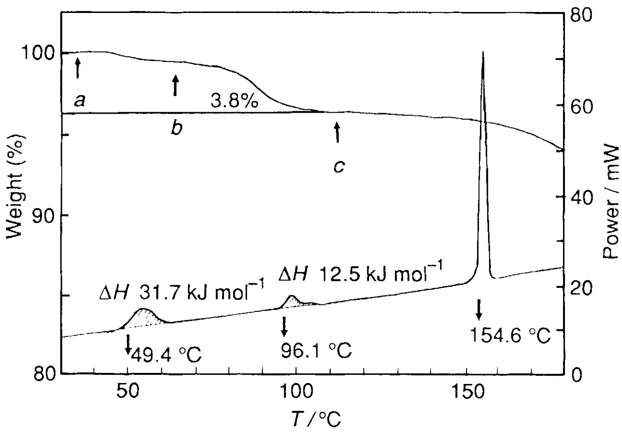

Fig. 2 TG and DSC curves for $Ph_3SiOH{\cdot}0.25\ EtOH$

hosts and two guests are located cyclically about a centre of inversion and are interlinked by hydrogen bonds with O · · · · O distances of 2.71 and 2.72 Å.

We have carried out thermal analysis on these two clathrate compounds and, for the $Ph_3COH{\cdot}MeOH$ compound, the experimental weight loss of 10.3% is in fair agreement with 10.96% required for the 1 : 1 compound. The corresponding differential scanning calorimetry (DSC) curve shows a skewed peak due to the endothermic loss of the MeOH. The area under this peak corresponds to the enthalpy of the guest release reaction, which is estimated to be ΔH 44.4 kJ mol^{-1}. The second peak with onset at 162 °C corresponds to the melting point of the host compound. The corresponding result for the $Ph_3SiOH{\cdot}0.25\ EtOH$ clathrate is more complex and is shown in Fig. 2. The thermogravimetric (TG) curve indicates that the ethanol is removed in two distinct steps, and the total measured weight loss of 3.82% is in good agreement with that required for the 4 : 1 complex (4.00%). The DSC curve shows two endotherms with onset temperatures of 49 °C (ΔH 31.7 kJ mol^{-1}) and 96 °C (ΔH 12.5 kJ mol^{-1}), while the third peak with onset at 155 °C corresponds to the melting of the triphenylsilanol.

The two-step decomposition reaction of the triphenylsilanol clathrate suggested the possibility of the formation of a new phase. This was established by X-ray powder diffraction. Fig. 3 shows the diffraction patterns of various forms of the triphenylsilanol–ethanol molecular complex: (*a*): after it had been freshly removed from its mother liquor and crushed (β-phase); (*b*): crushed and exposed to air until it had shown a 1.02% weight loss; (*c*): crushed and dried at 110 °C for 6 h *in vacuo*, which yields essentially the same pattern as Fig. 3(*d*), which is the pattern obtained from the pure host crystallised from diethyl ether, which is known to yield the non-porous α-phase. The X-ray powder pattern shown in Fig. 3(*b*) is different from the other patterns and corresponds to a new structure which we have labelled as the γ-phase.

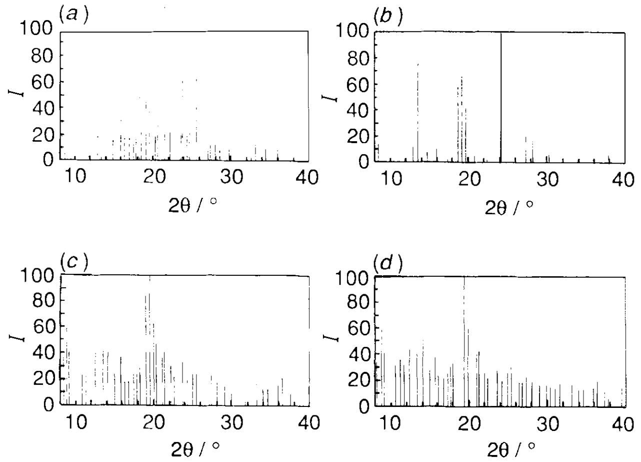

Fig. 3 X-Ray powder diffraction patterns of $Ph_3SiOH{\cdot}0.25\ EtOH$ at various stages of decomposition (see text): (*a*) β-phase; (*b*) after 1.02% weight loss; (*c*) after guest loss; (*d*) α-phase

A similar powder diffraction study of the triphenylmethanol compound shows that the structure of the host compound reverts to the initial non-porous α-phase after loss of guest.

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