SYNTHESIS OF LABELLED COMPOUNDS FOR ORGANIC SOLID STATE SELF-DIFFUSION STUDIES

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SUMMARY

The synthesis and purification of radioactively labelled forms of hexamethyldisilane, norbornylene [bicyclo(2,2,1)-hept-2-ene], norbornane [bicyclo(2,2,1)-heptane] and tert-butylmercaptan [2-methyl-2-propanethiol] is described.

INTRODUCTION

There is considerable current interest in the point defect nature and diffusion mechanisms in organic solids [1, 2].

Self-diffusion coefficients in organic solids vary considerably, being dependent on the type of solid. For example, the self-diffusion at the melting point, D_m, in aromatic crystals is typically 10^{-15} m^2 s^{-1} whereas for crystals of roughly spherical molecules, which form the so-called *plastic crystals* [3], D_m is typically 10^{-12} m^2 s^{-1}. A variety of experimental techniques have been used to study self-diffusion in organic solids, however, the most generally applicable and reliable is the tracer sectioning technique [1, 2]. In this experiment a very thin layer of radioactively labelled tracer is deposited on the surface of a pure single crystal, the crystal annealed at a constant temperature for a known time, sectioned parallel to the deposition surface and the specific activity of each section determined. From the penetration profile and the time of the anneal the diffusion coefficient can be evaluated [4]. When the tracer is not

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commercially available its preparation can be a serious problem and require a considerable research effort [5].

Self-diffusion in plastic crystals can be studied by nuclear magnetic resonance relaxation time measurements [1, 2] which combined with tracer studies can provide information on the diffusion mechanism [6, 7]. We have been using the two techniques to study self-diffusion in hexamethyldisilane [7], norbornylene [bicyclo(2,2,1)-hept-2-ene] [8, 9] , norbornane [bicyclo(2,2,1)-heptane] [8, 9]. In addition we have measured the self-diffusion coefficient as a function of pressure in hexamethyldisilane [9] and norbornylene [9]. We have also developed the tracer vapour exchange technique [2, 10] to study self-diffusion in *tert*-butylmercaptan [2-methyl-2-propanethiol][11]. In all this work a high specific activity of the tracer was not essential, in fact, since these materials are all votalile a high specific activity would present problems of contamination. As was emphasized by Lockhart [5], the major requirement was high purity of the tracer.

The syntheses of the tracers that were finally used were chosen for their simplicity i.e. the minimum number of reaction steps, and the absence or easy removal of unwanted side-products. These syntheses and subsequent purification procedures are described below.

EXPERIMENTAL

All the purities quoted were obtained by vapour phase chromatography [v.p.c.]. A variety of chromatograph column packings were investigated and it was found that a 10% silicone oil E 30 on Gas-Chrom Q [Applied Science Labs] column operated at 25°C was suitable for the analysis of all the materials, reagents and products, mentioned below.

(a) Hexamethyldisilane - ^{14}C

Inactive hexamethyldisilane was first prepared from trimethylchlorosilane by the method of Smith and Wilson [12]. This material was purified by fractional distillation [1 m column packed with glass helices] and zone-refining. The final product was of 99.995% purity, the major impurity being hexamethyl disiloxane.

Dry hydrogen chloride gas was bubbled through pure hexamethyldisilane at room temperature in the presence of a catalytic amount of aluminium chloride to produce methylchlorosilanes [13]. The reaction was followed by v.p.c. and was allowed to continue until the product was predominantly tetramethyldichlorodisilane. Mass spectral analysis confirmed the products were tetramethyldichlorodisilane [98%] and pentamethylchlorodisilane.

$$(CH_3)_3\ Si\ Si(CH_3)_3 + 2HCl \xrightarrow{AlCl_3} Cl(CH_3)_2\ Si\ Si(CH_3)_2Cl + 2CH_4$$

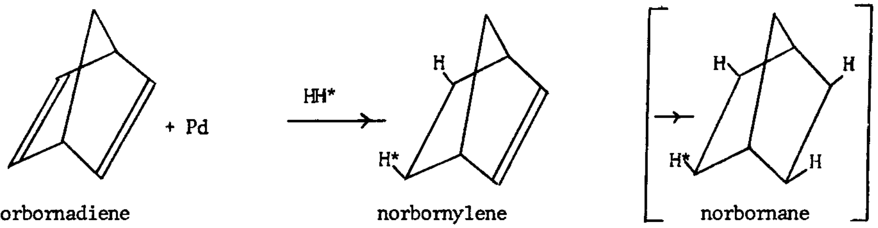
2.3 g [14 m mol] C^*H_3MgI, with a total activity of 100 µC, was prepared in ether by the standard Grignard procedure. 1 g [5.4 m mol] freshly prepared tetramethyldichlorodisilane in ether was slowly added to the stirred, cooled Grignard reagent, the excess Grignard deactivated and the hexamethyldisilane extracted in ether [14].

$$Cl(CH_3)_2\ Si\ Si(CH_3)_2Cl + 2C^*H_3MgI \longrightarrow (CH_3)_3\ Si\ Si(CH_3)_2(C^*H_3) + 2MgICl$$

The ether layer was washed, dried and the hexamethyldisilane obtained by distillation. Purification by four normal freezing procedures yielded 0.3 g [37% yield] hexamethyldisilane of 99.9% purity and a specific activity of 0.07 µC mg^{-1}. The dilute tracer conditions of the reaction meant that the active hexamethyldisilane molecules mostly contain only one ^{14}C. For use in the diffusion experiments the product was diluted with the pure, inactive material to a specific activity of ~0.01 µC mg^{-1}.

(b) Norbornylene 5 - ^3H

This synthesis employed the reduction of norbornadiene [bicyclo(2,2,1)-heptadiene] with tritium-hydrogen gas over a palladium catalyst and was based on the preparation of 5,6-dideuteronorbornylene described by Franzus et al [15]



Norbornadiene [Emanuel, reagent grade] was fractionally distilled [1 m column packed with glass helices] to yield material of 99.9% purity. 2 g of this material, 0.3 g 10% palladium on charcoal [Koch-Light] and 10 ml methanol were allowed to react with 500 ml tritium-hydrogen gas, at atmospheric pressure and room temperature, for 12 hours. The gas was prepared by reacting tritiated water [~0.2 C ml^{-1}] with calcium metal. The reduction mixture was filtered through glass wool into 15 ml water and the product extracted with three 10 ml portions of pentane. The combined extracts were dried over anhydrous sodium carbonate and the bulk of the pentane removed by distillation. V.p.c. analysis of this solution showed that there were approximately equal proportions of norbornadiene, norbornylene and norbornane. Franzus et al pre-treated the catalyst and obtained 86% norbornylene, 7% norbornane and 7% norbornadiene. Our attempts to pre-treat the catalyst and increase the yield of norbornylene were unsuccessful. However, we developed a very simple and effective purification using liquid chromatography.

The concentrated extracts were passed through an alumina column (30 mm i.d. x 1.2 m long packed with aluminium oxide, "Camag" M.F.C. neutral, 100-250 mesh) using pentane as the eluent. The 5 ml. fractions were analysed by v.p.c. and there was a reasonable separation, components being eluted in the order norbornane, norbornylene and norbornadiene. Repeated chromatography of the norbornylene rich fractions, usually about 5 passes through the column, yielded a sample with no detectable norbornadiene and 0.5% norbornane compared to the norbornylene content. The bulk of the pentane was distilled off this sample which contained 0.3 g [15% yield] norbornylene of specific activity ~10 μC mg^{-1}. 3 g inactive norbornylene [Fluka puriss grade which had been fractionally distilled on a 1 m column packed with glass helices] of 99.9% purity was added to the sample. The remaining pentane was removed by fractional distillation on a micro-Vigreux column. Vacuum sublimation yielded norbornylene of 99.9% purity, the major impurity being nortricyclene [an isomer of norbornylene], which was diluted to a specific activity of ~0.03 μC mg^{-1} for use in the diffusion experiments. The low tritium concentration used in the preparation meant that the tracer molecules were singly labelled.

(c) Norbornane 5 - ^{3}H

This synthesis was a simple extension of (b). Purified norbornylene was tritiated using the palladium catalyst. In this case the reaction was left for 24 hours at room temperature and any unreacted norbornylene was removed by further reaction with hydrogen. The reduction mixture was filtered into water and the norbornane extracted with pentane. The pentane was removed by fractional distillation on a micro-Vigreux column. After vacuum sublimation the product was of 99.99% purity. Again the tracer was diluted to ~0.03 μC mg^{-1} for use in the diffusion experiments.

(d) *tert*-Butylmercaptan - ^{35}S

The method adopted for the preparation of radioactive *tert*-butylmercaptan was that of Lee et al [16] and proceeded via the S-*tert*-butylthiouronium bromide.

$$(CH_3)_3COH + HBr + (H_2N)_2 : C : S^* \longrightarrow H_2\overset{+}{N}:C(NH_2)S^*C(CH_3)_3\ Br^- + H_2O$$

$$H_2\overset{+}{N}:C(NH_2)S^*C(CH_3)_3Br^- + NaOH \longrightarrow (CH_3)_3CS^*H + NaBr + H_2O + H_2NC\vdots N$$

18.5 g [0.25 mol] *tert*-butanol [Fisons laboratory reagent grade, fractionally distilled on a 1 m column packed with glass helices], 21 g [0.28 mol] thioruea [total activity 100 μC], and 0.28 mol 50% aqueous hydrobromic acid were heated for 30 minutes at gentle reflux. The mixture was cooled on an ice-bath, then the crystals of the thiouronium salt were filtered off and washed with 10% aqueous hydrobromic acid. The salt was dried under vacuum, powdered and added to an aqueous solution of 15 g [0.38 mol] sodium hydroxide containing a trace of sodium cyanide. This mixture was stirred under nitrogen for 12 hours. The mercaptan separated out as the upper layer and was removed by direct distillation. After washing the crude mercaptan with distilled water and drying over magnesium sulphate the pure product was obtained by fractional distillation through a 0.3 m column packed with glass helices. The yield was 10 g [40% yield] *tert*-butylmercaptan of 99.95% purity and specific activity 0.004 μCmg^{-1}. A high purity product from this synthesis was obtained since the major side-product, iso-butylene [2-methyl-propene] boils at -6.6°C and was easily removed.

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