NOTES

SYNTHESIS OF VINYL [^{36}Cl] CHLORIDE

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INTRODUCTION

The two most important reactions for preparation of vinyl chloride are (i) reaction of hydrogen chloride with acetylene in the presence of a catalyst which usually consists of a mercury salt on a support of active carbon or silica, or (ii) reaction of chlorine with ethylene to give 1,2-dichloroethane followed by elimination of hydrogen chloride (1). Variations on method (ii) have proved convenient for laboratory preparation of vinyl chloride (2) and one modification was used successfully to prepare pure [^{14}C]vinyl chloride from [^{14}C]ethylene (3).

The mechanism of the reactions involved in method (i) was investigated by Barton and Mugdan (4) and this suggested the synthetic procedure adopted in the present work. Reaction over a mercuric chloride catalyst is thought to proceed in two stages, the first involving formation of 2-chlorovinylmercurichloride (reaction 1) and the second, a decomposition of the intermediate by hydrogen chloride to give vinyl chloride and regenerate the catalyst (reaction 2). The intermediate

$$CH{\equiv}CH + HgCl_2 \longrightarrow CHCl{=}CH{-}HgCl \qquad (1)$$

$$CHCl{=}CH{-}HgCl + HCl \longrightarrow CHCl{=}CH_2 + HgCl_2 \qquad (2)$$

may be prepared by passing acetylene into an aqueous or alcoholic solution of mercuric chloride. Various procedures were tried and it was concluded that the best method was to use a saturated

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alcoholic solution containing 5-10% concentrated hydrochloric acid. This is the stage at which the label must be introduced as [^{36}Cl]chloride ions in the solution, though only half of the chlorine atoms become bound to carbon. Fortunately, reaction 2 does not result in any further loss of isotopic label as it has previously been shown that hydrogen bromide can be used to decompose the intermediate without formation of vinyl bromide (reaction 3) (5).

$$\mathrm{CHCl{=}CH{-}HgCl} + \mathrm{HBr} \longrightarrow \mathrm{CHCl{=}CH_2} + \mathrm{HgClBr} \qquad (3)$$

EXPERIMENTAL

Safety note. Chlorovinylmercurichloride was found to be an acute skin irritant and caused blistering. Rubber gloves were required for all operations when the compound was handled whether it was radioactive or not.

1. Preparation of 2-[^{36}Cl]chlorovinylmercurichloride

Mercuric chloride (28.25g; 0.104 mole) was dissolved in ethanol (95 ml, AR grade) and hydrochloric acid (4 ml, 10M) in a 250 ml wash bottle. Hydro-[^{36}Cl]chloric acid (1.23 ml, 0.1M, 100 μCi) was added and the solution stirred and allowed to stand for a period to allow complete equilibration of the isotopic label. Then purified acetylene gas was bubbled slowly through the solution at room temperature. Ethanol was added from time to time to replenish losses due to evaporation and a precipitate settled out during the course of the reaction. After 24 hours the entire contents of the wash bottle were transferred to a beaker containing cold water (400 ml) and stirred vigorously. The mixture was allowed to stand for 2 hours and then the precipitate collected by filtration and washed with distilled water until free from hydrochloric acid. The product was dried in a vacuum oven at 40^{o} to give a white powder (27.8g; 90% yield; Found: C, 8.1; H, 0.8 Calc. for $C_2H_2Cl_2Hg$: C, 8.1; H, 0.7%. mp 110-112^{o} -

literature mp data is confused due to the possibility of cis, trans isomerisms (4) but a value for mp 113° has been reported (6).

2. Preparation of vinyl[^{36}Cl]chloride

The preparation was carried out on a vacuum manifold. 2-[^{36}Cl]chlorovinylmercurichloride (22.2g; 0.075 mole) was placed in a two necked pearshaped flask containing a magnetic stirrer and fitted with a dropping funnel containing hydrochloric acid (20 ml; 10M). The flask was attached to the manifold and evacuated. A receiver, fitted with a spring loaded stopcock was also attached to the manifold via a column (15 x 1.5 cm) of 'Colorcarb' (Na_2O) granular absorbant and evacuated. The system was isolated from the vacuum pumps, and vinyl[^{36}Cl]chloride liberated by very slow addition of hydrochloric acid to the stirred intermediate. The labelled monomer was collected periodically after a moderate pressure had built up by cooling the receiver in liquid nitrogen and opening its stopcock for a moment or two. In this way evaporation of the hydrochloric acid was largely avoided. When the reaction was completed the reaction flask was replaced by a clean vessel and the vinyl[^{36}Cl]chloride dried and purified by several passes through the 'Colorcarb' column. (Yield: 3.81g; 82%).

3. Radiochemical assay

A portion of the vinyl[^{36}Cl]chloride was polymerized at 60° in dichloroethane solution using azobisisobutyronitrile as initiator. The polymer was isolated by precipitation in excess methanol, filtered and dried to constant weight in a vacuum oven at 40°. Small samples (5-10 mg) were dissolved in dimethyl sulphoxide (2 ml) in 20 ml scintillation counting vials. Fluor (5 ml; 1% butyl-PBD in toluene) and toluene (3 ml) were added and the vials counted in a Philips Liquid Scintillation Analyser at about 85% efficiency for [^{36}Cl]. The specific activity of the polymer was found to be 1.48×10^4 dpm. mg^{-1}, indicating an overall radiochemical yield of approximately 26% in reasonable agreement with the chemical yield of 74% which when corrected for available chlorine gives a value of 31%.

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