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PREPARATION OF [^{36}Cl]-CHLORINE LABELLED 1,1-DICHLOROTETRAFLUOROETHANE

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SUMMARY

The synthesis of [^{36}Cl]-chlorine labelled 1,1-dichlorotetrafluoroethane by the photolysis of 1-chloro-1,2,2,2,-tetrafluoroethane with [^{36}Cl]-dichlorine is described.

INTRODUCTION

The vapour-phase fluorination of chlorofluoroethanes by hydrogen fluoride over chromia catalysts is a subject of current interest in these laboratories [1,2] and in order to determine the role of surface chlorine in these reactions, a chlorofluoroethane labelled with [^{36}Cl]-chlorine was required. The obvious route to such compounds is by photolysis of a C-H bond in the presence of molecular chlorine [3,4] and the preparation of [^{36}Cl]-CCl_2FCF_3 from $CHClFCF_3$ by this route is now reported.

SYNTHESIS

[^{36}Cl]-chlorine labelled CCl_2FCF_3 is conveniently prepared by vapour phase, mercury-lamp photolysis according to equation (1)

$$CHClFCF_3 + [^{36}Cl]\text{-}Cl_2 \xrightarrow{h\nu} [^{36}Cl]\text{-}CCl_2FCF_3 + H^{36}Cl \qquad (1)$$

Labelled [^{36}Cl]-Cl_2 was prepared by oxidation of aqueous [^{36}Cl]-chloride ion, $Na^{36}Cl$ (1.9 MBq, Amersham International plc) diluted with concentrated hydrochloric acid (35cm^3), using aqueous potassium permanganate (300cm^3, 0.3 mol dm^{-3}). Traces of HCl were removed by passing [^{36}Cl]-Cl_2 through solid $KMnO_4$, the product was dried over phosphorus(V) oxide and stored in vacuo in a Monel metal bomb. The chlorine produced was sufficient for six photolytic syntheses.

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Photolyses of $CHClFCF_3$, $[^{36}Cl]$-Cl_2 mixtures were performed in an evacuable Pyrex bulb (2ℓ) using various mole ratios and irradiation times (8-68 h). Optimum conditions were a 36h irradiation time with $[^{36}Cl]$-Cl_2 in slight excess over that required by equation (1), $[^{36}Cl]$-Cl_2 205 Torr and $CHClFCF_3$ 195 Torr. The progress of a reaction was followed by monitoring i.r. spectral bands at 820 and 700 cm^{-1} due to $CHClFCF_3$, and at 735 cm^{-1} due to CCl_2FCF_3. $[^{36}Cl]$-Labelled HCl and unchanged Cl_2 were removed by treatment with moist NaOH pellets and the chlorofluoroethane product isolated in >90% yield. Found mol. wt. (vapour density) 171.3 ± 1.6; $C_2Cl_2F_4$ requires 170.9.

The products and reactants are easily differentiated by their ^{19}F n.m.r. spectra, Table 1.

TABLE 1

^{19}F N.M.R. spectra [a]

	$\delta(CF_3)$ [ppm]	$\delta(CF_2)$ [ppm]	$\delta(CF)$ [ppm]	$^3J(FF)$ [Hz]	$^2J(HF)$ [Hz]	$^3J(HF)$ [Hz]
CCl_2FCF_3	-84.2		-76.9	8		
$CClF_2CClF_2$		-71.1				
$CHClFCF_3$	-82.2		-157.0	10	48	4
CHF_2CClF_2		-133.7 -73.8		7	55	2

[a] Chemical shifts w.r.t. external CCl_3F.

N.m.r. analysis of the product indicated that the mole ratio CCl_2FCF_3 : $CClF_2CClF_2$ was 19:1 compared with the mole ratio $CHClFCF_3$: CHF_2CClF_2 = 24:1 in the starting material.

The specific activity of $[^{36}Cl]$-CCl_2FCF_3 prepared by this route is typically 6.1 MBq mol^{-1} corresponding to a radiochemical yield of approximately 33%. Specific activities were determined by liquid scintillation counting (Philips PW4700). A quenching curve, relating counting efficiency to the counter signal/channel ratio was determined by adding known quantities of CCl_2FCClF_2 to a standard volume ($2cm^3$) of scintillator (Packard Insragel). This relationship was used to correct observed [^{36}Cl]-count rates to an efficiency of 100%.

Specific count rates for reactant [^{36}Cl]-Cl_2 and product $H^{36}Cl$ were determined by Geiger Müller counting using an experimentally determined self absorption curve after conversion of the compounds to $Ag^{36}Cl$. The specific count rate of $H^{36}Cl$ obtained from a 36h irradiation was $(6.5 \pm 0.2)\times 10^4$ count s^{-1} (mol AgCl)$^{-1}$ compared with $(7.1 \pm 0.2)\times 10^4$ count s^{-1} (mol AgCl)$^{-1}$ determined for [^{36}Cl]-Cl_2 prior to reaction. Corresponding count rates for a 68h irradiation were $(3.2 \pm 0.1)\times10^4$ and $(3.9 \pm 0.1)\times10^4$ count s^{-1} (mol AgCl)$^{-1}$ for $H^{36}Cl$ and [^{36}Cl]-Cl_2 respectively. These results suggest that Cl-for-Cl exchange is a relatively unimportant route for [^{36}Cl]-chlorine incorporation in the product when shorter irradiation times are used.

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