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GLC AND RADIOMETRIC DETERMINATION OF HYDROLYSIS RATE CONSTANTS OF [[2-[4-(METHOXYCARBONYL) 1) BENZAMIDO]DIETHYL]TRIAMINO] METHYLATED POLYSTYRENE

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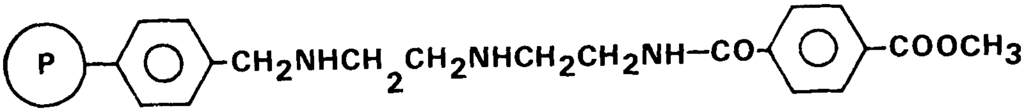
ABSTRACT

The rate constants of the hydrolysis of the methyl ester in 3N HCl as function of temperature was determined and found to be in the range of 1.3 x 10^{-2} to 1.2 x 10^{-1} h^{-1} at 40 and 60 C respectively. The rate constants were determined by GLC on Pola-pack-Q and by a radiotracer technique.

INTRODUCTION



Scheme I

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The [[2-[4-(methoxycarbonyl 1) benzamido]diethyl]triamino] methylated polystyrene (I) is an insoluble polymeric matrix and therefore the rate of hydrolysis of the methyl ester can be measured only determining the quantity of methyl alcohol released in the solution. Gas chromatography has been used to determine quantitatively the methly alcohol formed during hydrolysis reaction (1,2). Also, radiotracer techniques may be used for the same purpose. In this investigation the rate of hydrolysis of methyl ester in the presence of 3N HCl was determined by both GLC and a radiotracer technique. The GLC procedure used in this investigation has been reported previously (2,3).

EXPERIMENTAL

The synthesis of (I) is described in detailed in another paper. Briefly, the synthetic scheme involved the reaction of popcorn chloromethylated polystyrene (7.9% Cl) with diethylenetriamine which has been described previously (4,5). The polystyrene diethylenetriamine (5.1%N) was then reacted with 1,4 benzene dicarboxylic acid to form (I) which in turn reacted with CH_3ONa in methanol to form the methyl ester. The elemental analysis showed that the polymeric matrix contained one methyl ester group for every four styrene groups. The ^{14}C labeled ester was prepared by the same synthetic scheme using $^{14}CH_3ONa$ [2]. The specific activity of the polymer was 3 μCi/g.

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The gas chromatography procedure that was used in this investigation has been described previously (2). Briefly, a coiled stainless stell column (210 cm x 3 mm i.d.) packed with Pola-pack Q (150-200 mesh)[1] was placed in a gas chromatograph[1] with a flame ioniation detector. The column was preconditioned at 230 C for 24 hours and during the analysis it was kept at 160 C. The injection port and flame ionization detector were kept at 190 C. The flow rates for helium, hydrogen and air were 60, 45, and 200 ml/min, respectively.

One gram of the resin was placed in a beaker with 3N HCl (50 ml) under continuous stirring. One ml samples were withdrawn from the mixture at 0, 0.5, 1, 2, 3, 6, 9, 12, 18, 24, and 48 hours. Tertiary butanol[4] (internal standard) was added to each sample, and 0.5 μl of it was injected into the gas chromatograph. The samples were tested in triplicate. The peak heights of the methyl alcohol and internal standard were measured and their ratio was used to calculate the concentration of methyl alcohol by reference to a standard curve which was obtained by analysis of samples containing known quantities of methyl alcohol and internal standard.

The radioactive samples were counted in a liquid scintillation spectrometer.[3] Three hundred μl of the sample were placed in a liquid scintillation vial with solubilizer NCS (1.2 ml) and 18.5 ml of toluene scintillation cocktail (0.2 mM POPOP 27 mM PPO). All samples were corrected for counting efficiency using the channels ratio technique and tested in triplicate.

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RESULTS AND DISCUSSION

Both the gas chromatographic technique and the radioassay gave good estimates of the hydrolysis rate constants as it is shown in Table 1.

The total quantity of the methyl alcohol liberated over the 48 hours period of the experiment was used as the initial concentration, A_∞. Since the concentration of the water is very high, the hydrolysis is described by a pseudo-first order reaction. The apparent pseudo-first order rate constants at different temperatures in the presence of 3N HCl is shown in Table 1. The release of CH_3OH from the polymeric matrix after hydrolysis was unimpeded. Since the polystyrene resin cross-linked with 0.2% divinylbenzene contracts in the presence of aqueous media, the release from this matrix will depend on the rate of hydrolysis of the methyl ester bond which can be des-

TABLE 1

Apparent Pseudo-First Order Rate Constants

of Hydrolysis of Methyl Ester Bond

Temperature (C)	GLC Kapp.(h^{-1})	Radiometric Kapp.(h^{-1})	Average Kapp.(h^{-1})
40	1.47×10^{-2}	1.13×10^{-2}	1.3×10^{-2}
60	1.02×10^{-1}	1.41×10^{-1}	1.2×10^{-1}

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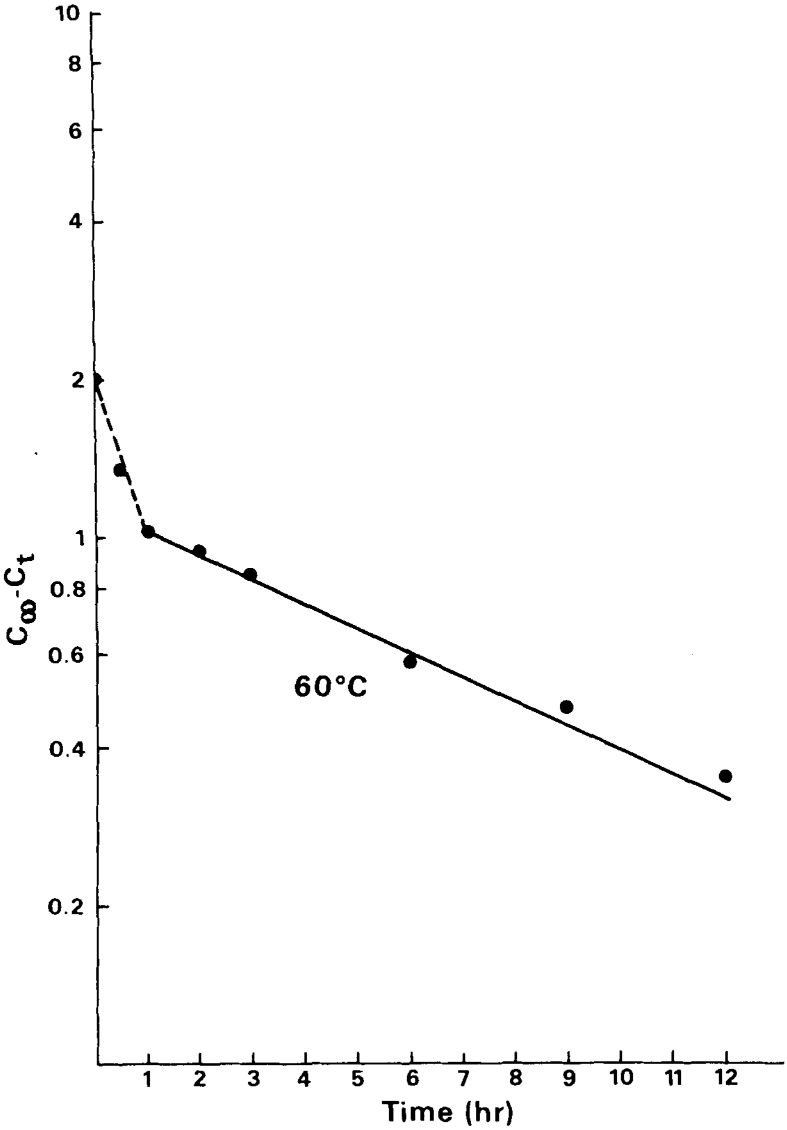

Figure 1. Infinity minus plot for the release of methyl alcohol from the resin in the presence of 3N HCl.

cribed by pseudo-first order kinetics and the rate of release of methyl alcohol from the matrix which is also described by pseudo-first order kinetics (6). The apparent pseudo-first order hydrolysis rate constant was determined from infinity minut plot (Fig. 1). The rapid initial decrease is due to the hydrolysis of methyl esters groups on the surface of the polymer matrix.

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FOOTNOTES

1. Water Associates, Inc. Milford, MA.
2. Gas Liquid Chromatographer Model Varian 1700.
3. Packard Tri-Carb Model 2002, Downers Grove, IL.
4. Fisher Scientific Co., 52 Faden Road, Springfield, NJ 07081.

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