Terephthalic acid from PET, by CHROMIUM

Introduction

Terephthalic acid can be made by saponification of polyethylene terephthalate (PET). Polyethylene terephthalate is a common polyester, readily available as plastic from drink bottles.

Saponification usually takes place if the ester is heated with hydroxides. For example we could take NaOH solution in water and heat PET pieces in it. This however is less practical as it takes hours or days to complete and the product is harder to separate. It was possible to saponify thin pieces of PET at room temperature within a month or less if a solution of a small amount of NaOH in 75% methanol was used. Saponification is trully fast if NaOH is dissolved in ethylene glycol and this solution is heated nearly to its boiling point (195...200°C). Description of a very similar process is given in [1].

$$\begin{aligned} \mathrm{C_6H_4(COOCH_2)_2 + 2NaOH} &\rightarrow \mathrm{C_6H_4(COONa)_2 + (CH_2OH)_2} \\ 192x + 80x &\rightarrow 210x + 62x \end{aligned}$$

Procedure

Reagents:

Ethylene glycol, 55 mL

NaOH, 12 g

PET, 22 g

5 mol/liter sulfuric acid solution, 30 mL

NaOH was taken with some excess over the theoretical amount. Ethylene glycol is just a solvent and does not take part in the reaction. 55 mL seemed a fair amount for this reaction.

The mixture of ethylene glycol, PET and NaOH was well stirred in a stainless steel beaker. The beaker was placed on a hotplate and heating applied.

The hotplate was switched off as soon as the mixture started to boil and was switched on again when boiling ceased. The boiling point of this mixture was near 200°C. The mixture was continuously stirred with a steel rod. This process lasted 20 minutes. During this time the liquid turned milk-white and pieces of plastic gradually decomposed.

The beaker was removed from the hotplate. After some cooling 200 mL water was added and the mixture was well-stirred. More water was added and stirring was continued to dissolve all solids. Even though there were some white pieces that had the inital shape of plastic parts, it all dissolved. Almost 400 mL water was needed to dissolve everything. The solution was filtered through a coffee filter.

5 mol/L sulfuric acid was added dropwise to the filtered solution. White precipitate at once appeared. The pH was checked and no more sulfuric acid was added when pH 2 was reached. The addition of sulfuric acid must be done in a well-ventilated area as some dioxane may be evolved. The testing of pH is not strictly necessary as the amount of sulfuric acid needed can be easily computed. One needs 0.5 mol of sulfuric acid for each mol of NaOH initially taken. The mixture was well-stirred and left to stand for 30 minutes.

The white precipitate was separated at first by filtration. It still contained a lot of liquid that was impossible to remove this way. Impure and wet terephthalic acid was placed together with filter paper onto a piece of strong cotton fabric. This fabric was folded as a bag and pressed hard until no more water separated. This crude terephthalic acid was mixed again with 500 mL water and separated by filtration and pressing to get a still-purer product.

Figure 1: Resin identification code 1 on plastic articles indicates polyethylene terephthalate

The yield of terephthalic acid is almost theoretical. Ethylene glycol can be recovered for re-use from the aqueous waste solution by boiling off water. Concentration must be performed in a fume hood as some dioxane may be formed because of the sulfuric acid.

Terephthalic acid is almost insoluble in water. When clean it is odorless. It is not deliquescent but somewhat hygroscopic. Heating is needed to dry it completely and remove the last traces of organic solvents.

Figure 2: Illustrated steps of terephthalic acid recovery

References

[1] A. Oku, L.-C. Hu, E. Yamada, Alkali decomposition of poly(ethylene terephthalate) with sodium hydroxide in nonaqueous ethylene glycol: A study on recycling of terephthalic acid and ethylene glycol. *J. Appl. Polym. Sci.*, **63**, 595 (1997).