Catalytic Oxidation of 4-t-Butyltoluene

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Abstract

The oxidation of 4-t-butyltoluene in glacial acetic acid by hydrogen peroxide in a process catalysed by cobalt(II) acetate tetrahydrate and sodium bromide has been studied with the aim of increasing the selectivity towards 4-t-butylbenzaldehyde.

The reaction mixtures were analysed by HPLC. Product identification was via the use of authentic compounds and retention times.

The oxidation of 4-t-butyltoluene using hydrogen peroxide yielded five measurable products, 4-t-butylbenzaldehyde, 4-t-butylbenzoic acid, 4-t-butylphenol, 4-t-butylbenzyl bromide, and 4-t-butylbenzyl alcohol. The major product was 4-t-butylbenzaldehyde. The selectivity with respect to 4-t-butylbenzaldehyde depended upon the temperature, addition time of oxidant, oxidant type and concentration, and the cobalt(II) acetate tetrahydrate and sodium bromide concentrations.

The effect of the temperature at which the reaction was operated was studied. It was found that the oxidation of 4-t-butyltoluene should be carried out at lower temperatures due to the instability of the hydrogen peroxide at the higher temperatures. The temperature 45 °C was chosen as an optimum temperature for a good yield of 4-t-butylbenzaldehyde.

Hydrogen peroxide, cobalt(II) acetate tetrahydrate, sodium bromide concentrations were examined for yields and selectivity towards 4-t-butylbenzaldehyde.

When hydrogen peroxide is added over 30 minutes the reaction is complted within the first 15 minutes. Similarly if hydrogen peroxide is added over 60 minutes, the reaction proceeds rapidly during the first 30 minutes. Over-oxidation to 4-t-butylbenzoic acid does not occur. It was also found that the rapid reaction was inhibited after an initial stage. There was no clear evidence that any of the products except 4-t-butylbenzaldehyde, which is the major product, or more than 1 mmol of 4-t-butyphenol inhibit further oxidation. Adding 100 mmol of water to the reaction mixture the formation of 4-t-butylbenzaldehyde decreased. An engineering solution to remove the product continuously seems required for process optimisation.

Using TEMPO as free radical trap and manganese(II) acetate, the system was completely unreactive and no products were observed.

It is concluded that although many oxidants can be used in oxidation of 4-t-butyltoluene, hydrogen peroxide is considered to be a good oxidant towards 4-t-butylbenzaldehyde which is an important flavour and fragrance intermediate for manufacture of the perfumery compound called Lilial (Lily of the Valley).

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