Substituted benzoic acids are very important materials in chemical and pharmaceutical industries and can be prepared by the oxidation of corresponding substituted toluenes. The transformation of substituted toluenes to substituted benzoic acids have been less reported. This conversion has been accomplished using a variety of reagents such as nickel-catalyzed benzylic oxidation, ceric ammonium nitrate in aqueus acetic acid, potassium bromate, selenium dioxide, chromylchloride, silver(II)oxide in phosphoric acid, potassium permanganate adsorbed on alumina.

Since oxygen is highly soluble in subcritical water, it is one of the most attractive oxidants. The increasing environmental concern surrounding the use of toxic and dangerous oxidants has impelled organic chemists to develop oxidation methodologies using molecular oxygen.

The oxidation of toluenes to benzoic acids by molecular oxygen was reported to use several organic solvents, which is not desired environmentally friendly. Thus, there is a need to develop procedures for benzylic oxidation, which use inexpensive oxidizing agent and minimize the use of chromium complex.

Although pyridinium chlorochromate (PCC) oxidations are routinely performed in organic transformations the requirement of at least a stoichiometric amount of pyridinium chlorochromate to complete the oxidation is disadvantage due to the high toxicity of chromium reagents. Therefore, new methods for oxidations of toluenes to corresponding benzoic acids and that generate less chromium waste are still needed.

In our previous study, we have reported the oxidation of toluenes to aromatic aldehydes with molecular in subcritical water. In continuation of our work oxidation reactions of substituted toluenes, we now wish to report using a less catalyst an alternative procedure for this transformation.

Melting points were determined on an Electrothermal 9100® apparatus. IR spectra were recorded on a Win First Satellite® model spectrophotometer. $^1$H NMR spectra were obtained using a 400 MHz Bruker DPX® instrument.

Oxidations were carried out at 120 °C and in a 280 cm$^3$ stainless steel pressure reactor equipped with N$_2$ and O$_2$ inlet, pressure gauge, safety valve, digital temperature reader, heater and magnetic stirrer. The total pressure was kept at 60 bar by N$_2$. A glass vessel was inserted into the reactor to avoid the catalytic effect of steel and corrosion. The reactor was charged with toluenes and 270 mL H$_2$O. All the valves of the reactor were tightly closed during preheating. Nitrogen was supplied through a tube into the liquid phase directly. Then the desired oxygen pressure was applied to the vessel through a stainless steel tube into the liquid phase directly and the total reaction time was 2 h. After the reaction was completed, the reactor was cooled to room temperature and the reaction mixture was extracted with ethyl acetate (3 × 15 mL). The combined organic layer was dried (MgSO$_4$) and evaporated on a rotary evaporator under reduced pressure. Evaporation of the solvent gave fairly pure solids, which were crystallized from ethyl acetate; the melting point of solid compounds was checked and the solids were identified by IR and $^1$H NMR.

We report herein a facile and efficient oxidation of substituted toluenes to aromatic carboxylic acid. Using molecular oxygen in the presence of 1 mol % of pyridinium chlorochromate in subcritical water at 120 °C, we have oxidized electron-withdrawing and electron-donating substituted toluenes to carboxylic acids in excellent yields (Scheme-I).
In the present work, molecular oxygen is used to oxidize toluenes to their corresponding carboxylic acids in subcritical water. The dramatic decrease in solvent viscosity and an increase in substrate solubility suggest that subcritical water may be useful as a replacement for environmentally unacceptable solvents for a number of organic reactions.

The amount of dissolved oxygen in water at atmospheric pressure was determined according to Henry’s Law (at 25 °C the solubility of O₂ is of 1.296.10⁻³ mol/kg H₂O).

This value was used initially as shown in the Table-1 as entry A. The amount of oxygen was regulated by the oxygen pressure. All oxidations were performed by adding 280 mL water, one equivalent of substrate and two equivalents oxygen. Since longer reaction times did not improve the yields, the time was optimized at 2 h for all oxidations. On the other hand, when oxygen pressure was increased, the yields increased not beyond 20 bar; an increase in the amount of oxygen led to decomposition of the starting materials converting them to tars. All the products were characterized by their spectral data and comparison with reported data. The high-pressure and high-temperature system was used in all reactions.

Various substituted toluenes were oxidized in the presence of molecular oxygen with pyridinium chlorochromate mol % 1 in sub-critical water to give corresponding carboxylic acids mostly in quantitative yields and the results are shown in Table-1.

As can be seen from results (Table-1), toluenes substituted at the ortho or meta-position by electron withdrawing groups such as cyano and fluoro groups were oxidized smoothly to the corresponding benzoic acids in excellent yields (entries 4, 5 and 6, 8). Toluenes substituted by electron rich substituents (entries 2, 10 and 11) also undergo oxidation efficiently.

In conclusion, we developed a practical procedure for the oxidation of substituted toluenes to their corresponding substituted carboxylic acid in subcritical water with molecular oxygen with small amount metal catalysts.

ACKNOWLEDGEMENTS

The author is greatful to Mersin University Research Council and TUBITAK (The Scientific and Technical Council of Turkey) for the supporting this work (Grant No: TBAG-2235).

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