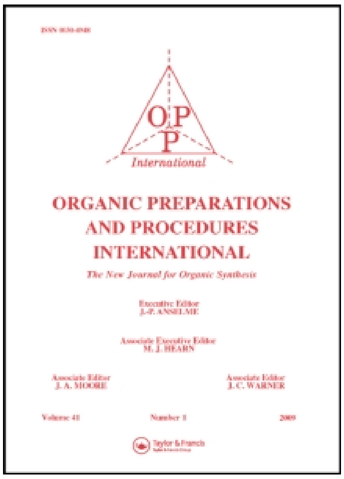

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OXIDATION OF TOLUENES TO AROMATIC ALDEHYDES WITH MOLECULAR OXYGEN IN SUBCRITICAL WATER

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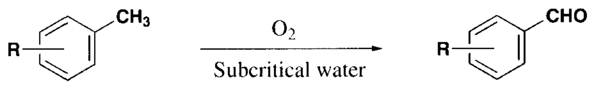
Oxidations are important transformations in organic synthesis.[1] In general, many oxidations are carried out with a large excess of chromium or manganese reagents. The metal residues are environmentally undesirable and often cause problems during work-up.[2] In addition organic oxidations in the chemical industry have traditionally been performed in either aromatic or halogenated solvents.[3] One of the most attractive oxidants is molecular oxygen,[4] since oxygen is highly soluble in subcritical water. Molecular oxygen has been used as the reagent for the oxidation of alkyl aromatic compounds in the presence of different catalysts, such as $MnBr_2$, $CoBr_2$,



R: –CN, –F, Cl, –Br, $-CH_3$, CH_3O

MnO_2.[4] The oxidation products, aromatic aldehydes, are important intermediates for the perfume, pharmaceutical, dyestuff and agrochemical industries. They are generally produced by hydrolysis of benzal chlorides and are also generated side-products of the liquid phase oxidation of toluenes to benzoic acids.[5] The present work uses subcritical water as solvent for oxidations. The dramatic decrease in solvent viscosity, increase in substrate solubility, and enhanced sensitivity of solvating properties suggest that subcritical water may be useful as a replacement for environmentally unacceptable solvents for a number of organic reactions.[6] This paper reports oxidation of substituted toluenes by different amounts of molecular oxygen in subcritical water in absence of catalysts.

The oxidation of methylbenzenes, *e. g.* toluene, *o*-xylene, *m*-bromotoluene, *m*-fluorotoluene, *p*-clorotoluene, *m*-cyanotoluene, *p*-methoxytoluene, was investigated in subcritical water as isothermal experiments at 150°C in different amounts of oxygen. The influence of both electron-withdrawing (–CN) and electron-donating groups (–F, –Cl, –Br, $-CH_3$, $-OCH_3$) was investigated. Preliminary results indicated, however, that under the proper conditions the desired products can be isolated in high purity and good yield (*Table 1*).

Table 1. Reaction Conditions and Yields for the Subcritical Water Oxidations

Reactant	Product[d]	mp/°C	bp/°C	Yield (%) at Oxygen pressure (bar)[a,b]				
			bp/°C	A[c]	5	10	15	20
Toluene	Benzaldehyde		181(*lit*[8] 179)	25	28	32	36	40
o-Xylene	*o*-phthalaldehyde	56(*lit*[8] 56)		27	29	34	40	42
	2-Methylbenzaldehyde		202(*lit*[8] 200)	10	12	15	17	20
m-Bromotoluene	*m*-Bromobenzaldehyde		231(*lit*[8] 229)	35	40	43	47	49
m-Fluorotoluene	*m*-Fluorobenzaldehyde		89 (*lit*[8] 90) (46 mmHg)	36	42	44	47	48
p-chlorotoluene	*p*-Chlorobenzaldehyde	48(*lit*[8] 46)		35	38	42	45	49
m-Cyanotoluene	*m*-Cyanobenzaldehyde	79(*lit*[8] 77)		40	43	48	52	55
p-Methoxytoluene	*p*-Anisolaldehyde	-1(*lit*[8] -1)		27	29	32	35	38

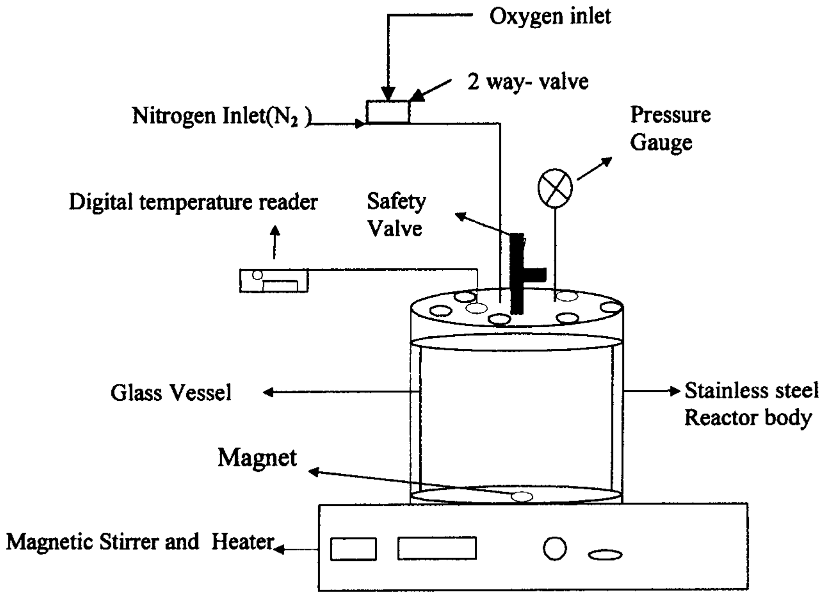
a) Double equivalents of molecular oxygen 5 bar, 4.63 x 10^{-3} mol/L 10 bar, 9.26 x 10^{-3} 15 bar, 1,38 x 10^{-2} mol/L 20 bar, 1.85 x 10^{-2} mol/L; b)Relative yield based on quantitative analysis; c) A: Disolved oxygen in water at atmospheric pressure 1,26 x 10^{-3}mol/L; d) All products were characterized by IR and H NMR spectroscopic data and their physical data compared with literature datas[8] Reaction conditions: Total pressure 40 bar, temperature 150°C

In this study, the highest yield was obtained from oxidation of cyanobenzene, since the cyano group withdraws electrons from the aromatic ring especially if it is in the *meta* position, and also oxidation is easy at the *meta* position.

The amount of dissolved oxygen in water and at atmospheric pressure was determined according to *Henry's Law*[7] (at 25°C the solubility of oxygen is of 1.296 x 10^{-3} mol /kg of H_2O)

and this value of oxygen was used initially as shown in the *Table 1* as A. The amount of oxygen was regulated by the oxygen pressure.[7] All oxidations were performed by adding 280 mL of water, one molar equivalent of substrate and two molar equivalents of oxygen. Since longer reaction times resulted in no change to 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 as they were converted to uncharacterized various tars (*Table 1*).

Although the mechanism of the oxidation of substituted toluenes by molecular oxygen in the presence of metal catalyst is known,[3] oxidation products may vary depending on reaction conditions such as pressure, temperature, time and catalyst. All the products synthesized were characterized by their spectral data[8] and known compounds by comparison with reported data.[8] We have developed a practical procedure for the oxidation of substituted toluenes to corresponding aldehydes in subcritical water with molecular oxygen in the absence of metal catalysts. It is noteworty that the reaction systems are applicable for the oxidation of electron-withdrawing and electron-donating substituted toluenes. The possibility of the recyclization of water and the absence of any catalyst, and controlling the reaction product by temperature and pressure make this method clean, inexpensive and valuable from an environmental point of view.



Schematic Illustration of the Oxidation System

EXPERIMENTAL SECTION

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker 400-100 MHz spectrometer, and infrared spectra were obtained as films on NaCl plates for liquids and KBr pellets for solids on Win First® Satellite Model infrared recording spectrophotometer. All column chromatography was performed on silica gel (60-mesh, Merck).

General Procedure.- Oxidations were carried out at 150°C and in a 280 mL stainless steel reactor[9] (*Fig. 1*). The total pressure was kept at 40 bar by N_2. A glass vessel was inserted in the reactor and the oxidation occurred without contacting the stainless steel reactor surface in order to avoid the catalytic effect of steel and corrosion. The reactor was charged with the organic compound and 280 mL of water. The reactor was heated to a desired temperature from the bottom by heater and surrounded by heat resistant material to protect from the loss of heat and temperature. 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 mixture was cooled to room temperature and washed with ether. The products were purified by column chromatography on silica gel (60-mesh, Merck with 50 cm glass column).

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