The Use of Cobalt(II) Ion and Hydrochloric Acid as Catalyst for the Liquid-phase Oxidation of Alkylbenzenes

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Summary The combination of cobalt(II) ions and hydrochloric acid is shown to be an excellent catalyst system for the oxidation of alkylbenzenes provided a mixed solvent consisting of chlorobenzene–acetic acid is employed

THE oxidation of alkyl-aromatic compounds to aromatic carboxylic acids using cobalt salts and a source of bromide ion in acetic acid is the basis of at least one important industrial process and numerous publications It has been reported[1] that chloride ion in contrast to bromide does not promote such cobalt-catalysed oxidations More recently it was demonstrated[2] that LiCl increases the rate of reaction of alkyl-aromatics with cobalt(III) acetate in the absence of oxygen in acetic acid

We have found that cobalt(II) acetate–HCl is an excellent catalyst for the oxidation of *p*-xylene or *p*-toluic acid to terephthalic acid in chlorobenzene–acetic acid at 176° Results are shown in the Table

TABLE

Yield of terephthalic acid as function of catalyst and solvent at 176°[a]

Experiment	Starting materials	Catalyst[b]	Time (h)	Solvent, PhCl (ml)	HOAc, (ml)	Yield terephthalic Acid,[c] (%)
1	*p* Xylene	A	1	45	30	93
2	*p*-Xylene	A	1		75	15
3	*p*-Toluic acid	A	2	45	30	94
4	*p* Xylene	C	2	45	30	45
5	*p* Xylene	B	1		75	94
6	*p* Xylene	B	1	45	30	92

[a] Reactions carried out in a 500 ml Parr Titanium Rocking Autoclave using 0 36 mol O_2, 0 36 mol N_2 as oxidizing gas and 73 4 mmol starting materials

[b] A 1 mmol $Co(OAc)_2$ $4H_2O$, 2 mmol HCl, B 1 mmol $Co(OAc)_2$ $4H_2O$ 1 mmol NaBr, C 1 mmol $Co(OAc)_2$ $4H_2O$

[c] Yield is obtained by g l p c analysis of an esterified portion of the dry reaction products, assuming complete conversion

Experiments 1 and 4 show the importance of HCl The mixed solvent is essential for the chloride catalyst (Expts 1 and 2), whereas in the bromide system (Expts 5 and 6) it is not Chlorobenzene alone is unsatisfactory as a solvent

The oxidation of *p*-t-butyltoluene using cobalt(II) acetate–NH_4Br at 90° has been shown to give *p*-t-butylbenzoic acid in >95% yield[3] The oxidation of *p*-t-butyltoluene (3 37 × 10^{-2} mol) at 182° in chlorobenzene–acetic acid with oxygen (0 22 mol) for 2 h using the bromide system (catalyst B) gave a 94% yield of *p*-t-butylbenzoic acid and <1% terephthalic acid Using the chloride system (catalyst A), the following products and yields were obtained *p*-toluic acid (6%), *p*-methylacetophenone (10%), *p*-t-butylbenzoic acid (30%), terephthalic acid (8%), and *p*-acetylbenzoic acid (17%)

t-Butylbenzene (5 69 × 10^{-2} mol) is inert to oxidation using the bromide system (catalyst B) in acetic acid (75 ml) and oxygen (0 22 mol) at 182° for at least 3 h,† however, using the chloride system (catalyst A) in the mixed solvent, only 52% of the t-butylbenzene is recovered after 3 h, and the major oxidation products are acetophenone and benzoic acid in 48 and 16% yields, respectively, based on converted t-butylbenzene

All oxidation products were identified by comparing g l p c retention times of their methyl esters (in the case of acids), m p, n m r, and i r spectra with authentic samples

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† The mixed solvent was not used to preclude the possibility of traces of chloride in the system from possible chlorobenzene decomposition

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