Copper-catalysed *para*-Carboxylation of Phenol by Carbon Tetrachloride in the Presence of Concentrated Sodium Hydroxide

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The orientation of attack of trichloromethyl cation (generated by copper catalyst from carbon tetrachloride) on phenolate was found to be strongly dependent on the concentration of the aqueous sodium hydroxide used, and practically selective *para*-carboxylation was observed under very mild conditions and with high isolated yield; addition of polyethylene glycol to the system also had a significant effect on the selectivity.

The carboxylation of phenol by carbon tetrachloride under alkaline conditions was originally reported by Reimer and Tiemann[1] [equation (1)]. The critical catalytic effect of copper metal on this reaction was reported later.[2] The main disadvantage of this method, as compared with the Kolbe–Schmitt carboxylation,[3] is the low selectivity and yield.

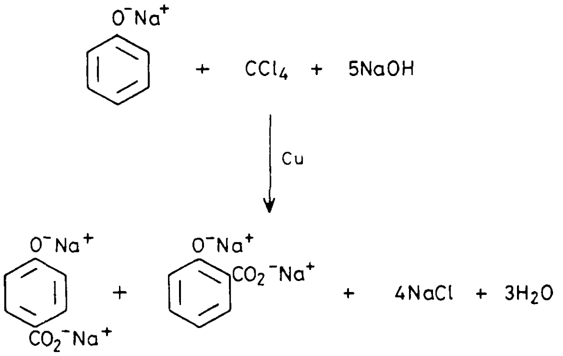
Komiyama and Hirai have recently observed that in the presence of β-cyclodextrin (5 mole% relative to phenol) reaction (1) takes place with 92% yield and 99% selectivity for formation of the *para*-isomer.[4,5] The selective mechanism was attributed to the formation of an intermediate ternary molecular complex between the β-cyclodextrin, phenolate anion, and trichloromethyl cation which induce a geometrical discrimination between the *para*- and *ortho*-positions on the phenolate ring.

We have now found that similar selectivity can be obtained in reaction (1) simply by careful control of the amount of water and sodium hydroxide in the system.

In an optimal procedure phenol (0.64 mol), sodium hydroxide (5.76 mol), water (230.4 g), and copper powder (15 mmol) were heated at 80 °C with efficient stirring, and carbon tetrachloride (0.66 mol) was added during 5 h in such a rate as to keep the reaction in gentle reflux. Every 2 h additional copper powder (0.6 g) was added. After a total of 6 h the mixture was cooled to room temperature and filtered, the filtrate acidified to pH 2 with concentrated hydrochloric acid and the solid crude product filtered off. Recrystallisation (×2) from water (with active carbon) gave 4-hydroxybenzoic acid, m.p. 213—214 °C (yield 86.5% based on the phenol), 99% pure by gas chromatography.

The main factor determining the selectivity (though not the rate) is the aqueous concentration of the sodium hydroxide. Thus, using a stoicheiometric quantity of sodium hydroxide (3.84 mol) and starting with different initial amounts of water forming 20, 33, 50, and 70% w/w aqueous sodium hydroxide, the measured ratio of 2- to 4-hydroxybenzoic acid in the isolated product was 0.78, 0.14, 0.063, and 0.086 respectively with the total recovered yield of carboxylated product remaining practically the same. Increasing the initial amount of sodium hydroxide used to 5.76 mol (50% excess) resulted in a further improved *ortho* to *para* ratio of 0.005. It is apparent that an initially 50% w/w sodium hydroxide solution, preferably in 50% molar excess, gives the highest selectivity.

The reacting system is heterogeneous, and contains four phases: aqueous phase, organic phase, solid copper powder, and precipitated solid sodium chloride. We were able to determine that, with sufficiently efficient mixing, the rate is first order in phenolate anion and in the copper catalyst. The rate is independent of the mole fraction of HO^-, Cl^-, carbon tetrachloride, and the product hydroxy acids. The copper catalyst was deactivated during the reaction and unless fresh batches were added while the reaction proceeded, the process stopped after a certain conversion (*e.g.*, in the above procedure after 60% conversion). Copper(II) and copper(I) salts or oxide were practically inactive as catalysts.



(1)

We suggest that the reaction takes place on the surface of the copper catalyst where the trichloromethyl cation is formed.[5] The highly concentrated aqueous solution appears to induce a certain degree of geometrical organization on the copper–aqueous interphase which forces the phenolate anion to approach the catalyst in such a way that the *para*-position is attacked preferentially. Since the composition of the aqueous phase changes as the reaction proceeds the measured final selectivity is the average of selectivities for the various stages of the process. Since with an initially 70% solution lower selectivity was observed, it can be concluded that an optimal composition exists where the selectivity is at a maximum.

The effect of the aqueous phase composition on the selectivity of reaction (1) can also be applied with the β-cyclodextrin catalysis. It can be argued that in addition to its function as a shape-selective catalyst *via* complex formation, the cyclodextrin also forms regions with high local concentration of base. This effect is possible only with cyclodextrins containing free hydroxy groups which can either be deprotonated or form hydrogen-bonded complexes with hydroxide anion. It was clearly demonstrated that when the free hydroxy groups are blocked by methyl substituents the cyclodextrin is not catalytically active.[5]

We were able to obtain similar effects by addition of catalytic amounts of polyethylene glycol (PEG; M_r 400). Thus addition of PEG-400 (16 g, 0.04 mol) in the above procedure, using 20% sodium hydroxide (3.84 mol), changed the *ortho*/*para* ratio from 0.78 to 0.41. The same amount of PEG-400 with 50% sodium hydroxide (3.84 mol) changed the *ortho*/*para* ratio from 0.063 to 0.006. PEG is known to form complexes with various salts[6] and was applied as a phase-transfer catalyst in numerous reactions, particularly in the presence of hydroxide base.[7] We have recently shown that a PEG–KOH complex forms a third liquid phase in the aqueous KOH–toluene system in which an isomerization reaction took place.[8] Similar complexation accompanied by 'localization' of the hydroxide base is probably involved in the carboxylation (1) in the presence of PEG as well.

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