

REDUCTION OF NITROBENZENE BY DODECACARBONYL TRI-IRON UNDER TRIPHASE CONDITIONS

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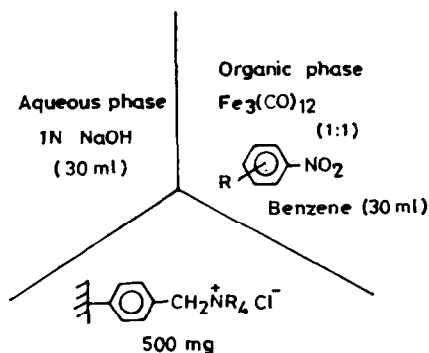
Summary

Reduction of nitrobenzene to aniline by $\text{Fe}_3(\text{CO})_{12}$ under triphase conditions has been investigated and the efficiency of the polymer-supported phase transfer agents compared. Reduction occurs under mild conditions and the isolation of the product is easier than in the homogeneous system. The yield of aniline is similar to that obtained in the $\text{Fe}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$ system.

Introduction

Applications of iron carbonyls to organic synthesis by phase transfer catalysis have been reported in several publications and have been reviewed extensively [1 - 3]. Phase transfer catalysis suffers from the same disadvantage as reactions in homogeneous systems, namely the difficulty in isolation of the product and separation of the catalyst. Binding the catalysts to insoluble resins as catalysts for biphasic reactions is an attractive concept, since in principle it allows repeated use of the catalyst and provides a simple method for its removal [4 - 9]. Regen has done pioneering work in anchoring onium salts to polystyrene resins and named the use of such systems 'triphase catalysis'.

Recently we have reported [10 - 12] the use of iron carbonyls in the reduction of ketones and nitroarenes under liquid-liquid biphasic conditions. However, the use of organometallic compounds under triphase conditions has not been described thus far. We report here the reactions involving dodecacarbonyltri-iron under triphase conditions for the reduction of nitrobenzene. The triphase system is represented in Scheme 1. Procedures [13] similar to those described for the quaternisation of chloromethylated polystyrene with *N,N*-dimethyl-*n*-butylamine were followed for the preparation of all polymeric catalysts. The tertiary amines used here are triethylamine, tributylamine and *N,N*-dimethylaniline. The polymeric catalysts have been well characterized by IR spectroscopy and their chlorine contents have been estimated by the procedure reported in the literature [14].



Scheme 1.

The reaction mixture was stirred under nitrogen atmosphere. The appearance of a wine-red colour, indicating the formation of the anion $[\text{HFe}_3(\text{CO})_{11}]^-$, took place after a longer time than under biphasic conditions at room temperature. The polymer beads were pretreated with benzene and the reactions carried out at temperatures between 40 and 45 °C. In this case the wine red colour appeared sooner than in the earlier procedure. Using all four polymer-anchored PTC agents, the reduction of nitrobenzene by $\text{Fe}_3(\text{CO})_{12}$ (1:1) was attempted and the yields of aniline formed determined by spectroscopic methods [15]. The results are presented in Fig. 1.

Results and discussion

Our studies suggest the following:

- (1) The yields are found to be lower than those reported under biphasic conditions [12].
- (2) As the bulkiness of the trialkylamine increases, there is a decrease in the percentage yield of the product. It is possible that the quaternary ammonium hydroxide cannot readily attack the neutral metal carbonyl to produce the hydrido-iron carbonyl species due to steric factors. As a result, formation of the hydridocarbonylate anion is very slow (indicated by the very slow change of colour from green to red).
- (3) Anchoring the PTC to 50% crosslinked polymer gives less yield of the product than anchoring the catalyst to 2% crosslinked polymer.
- (4) PTC is recovered by filtering and can be used repeatedly. This is particularly advantageous when costly crown ethers are used as PTC.
- (5) Upon treatment with 10% HCl overnight, the catalytic activity is regenerated. The regenerated catalyst gives the same activity as the fresh catalyst.
- (6) Anchoring of the metal carbonyl to the polymer support is indicated by change in colour from colourless to brown.

A separate experiment was carried out with no added substrate. After 8 h the catalyst was filtered, washed and dried. The IR spectrum of the com-

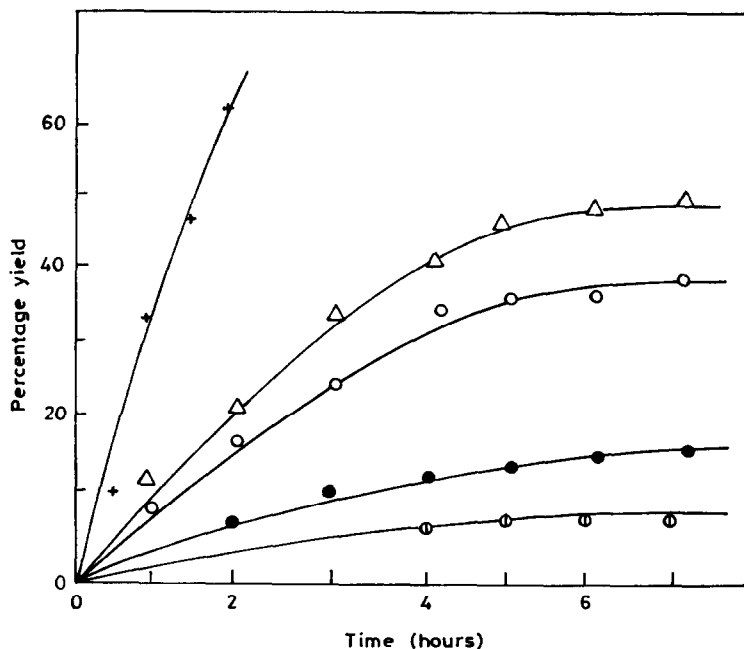
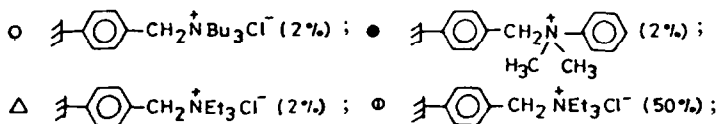


Fig. 1. Reduction of nitrobenzene by $\text{Fe}_3(\text{CO})_{12}$ under triphase conditions using various polymer-anchored PT agents. In all cases Fe = 16.64% by weight.



+ under biphasic conditions for benzyltriethylammoniumchloride as PTC. The number in parentheses is the crosslink density of the polymer.

pound was compared with that of $[\text{Et}_3\text{NH}][\text{HFe}_3(\text{CO})_{11}]$, and the results are given in Table 1. From this we can infer that $[\text{HFe}_3(\text{CO})_{11}]^-$ is coordinated to the polymer-anchored PTC. The IR spectrum is in agreement with the values reported by Effa *et al.* [16].

TABLE 1

Comparison of IR spectra of the anchored trinuclear species with that of unanchored species

Sample	$\nu(\text{CO})$ (cm^{-1})
$[\text{Et}_3\text{NH}][\text{HFe}_3(\text{CO})_{11}]$ in CH_2Cl_2	2070(w), 2000(vs), 1977(s), 1718(m)
$\text{---} \text{C}_6\text{H}_4 \text{---} \text{CH}_2 \text{N}^+ \text{Et}_3, [\text{HFe}_3(\text{CO})_{11}]^-$ in KBr	2060(w), 2000(vs), 1947(m), 1720(m)

Interaction of $\text{Fe}_3(\text{CO})_{12}$ [17 - 20] with the surface of alumina results in the formation of the anionic hydrido carbonyl cluster, $[\text{HFe}_3(\text{CO})_{11}]^- \text{M}^+$, ($\text{M}^+ = \text{Al}(\text{O})_x^+$). In the present investigation, in a typical experiment alumina (10 g) was heated for 8 h at 150 °C under reduced pressure. $\text{Fe}_3(\text{CO})_{12}$ (1.01 mmol) in degassed dry hexane (50 ml) and the activated alumina were stirred at room temperature under nitrogen atmosphere. Within 2 h the initially green solution turned colourless, and the solid became deep red. The IR spectrum of the solid showed bands corresponding to that of $[\text{HFe}_3(\text{CO})_{11}]^-$.

The trinuclear iron hydride, $[\text{HFe}_3(\text{CO})_{11}]^-$, supported on alumina was stirred with an equimolar amount of nitrobenzene for ~8 h at room temperature under nitrogen atmosphere. The aniline formed was estimated spectrophotometrically. It was observed that the trinuclear iron hydride supported on a sample of alumina prepared as described in the literature [21] was more active (yield of aniline is 75%) than a catalyst made with a sample of commercial BDH alumina as support (yield of aniline is 58%). The percentage yield of aniline formed with $\text{HFe}_3(\text{CO})_{11}^-$ anchored to alumina is comparable with the yield obtained under triphase conditions using $\text{PhCH}_2\text{NEt}_3\text{Cl}^-$ (as PTC) anchored to 2% crosslinked styrene divinylbenzene.

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