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Metal-assisted reactions, Part 31 [1]: Adsorption isotherms and selective catalytic transfer reduction of aldehydes and ketones

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Abstract

Heterogeneous catalysis of transfer reduction was assessed by measurement of liquid-phase adsorption isotherms, enabling quantitative evaluation of H-donor, H-acceptor and solvent interplay at the catalyst surface so as to find the optimum reaction conditions. Liquid-phase isotherms were measured for adsorption of aromatic aldehydes (H-acceptors) onto a commercial Pd/C catalyst from a range of solvents. The resulting isotherms provided fundamental information on the competitive adsorption of aldehyde and solvent molecules at sites on the catalyst surface. These results suggested a novel solvent system for the heterogeneously catalysed transfer reduction of aromatic aldehydes to alcohols. This new solvent system performs heterogeneously catalysed transfer reduction of aromatic aldehydes at room temperature in a highly selective way, thus, avoiding the previously proposed unselective processes requiring high temperatures. The heterogeneous catalyst was re-usable at least five times without any loss of activity. A major role of oxygen as a reverting inhibitor of transfer reduction was demonstrated.

Keywords: Heterogeneous catalysis; Transfer hydrogenation; Mechanism; Adsorption isotherms; Liquid phase; Aldehydes; Reduction

1. Introduction

Heterogeneous catalysis in the liquid phase provides easy fast hydrogenation or hydrogenolysis of a variety of functional groups under mild conditions and without the need for hydrogen gas [2]. Remarkably, the carbonyl group in aldehydes and ketones resists reduction in heterogeneous phase-transfer methods, with an exception of a few cases, where extreme conditions were used [3]. More recently, the interest in this area has been renewed by the regio- and chemo-selective reduction of carbonyl groups over nickel-containing silicates and cobalt-containing aluminium phosphates [3,4]. Homogeneous catalytic methods of hydrogen transfer reduction of the carbonyl group have been used successfully, although the expensive soluble catalysts requires a complicated recovery process in all cases but the small-scale research [5]. Because of economic and practical difficulties raised by the available catalytic methods, carbonyl groups are more routinely reduced by a wide variety of soluble metal hydride reagents. Even so, the choice of metal hydride is crucial for achieving reasonable selectivity, additionally, such reactions normally require dry solvents and may involve conversion of an aldehyde to a derivative before its reduction [6].

In the present work, hydrogenation of aromatic aldehydes to primary alcohols was achieved at ambient temperatures and pressures under very mild conditions, using readily available and cheap hydrogen donors and easily recoverable and re-usable heterogeneous catalyst (Pd/C). The reaction proved to be very selective over a range of carbonyl groups. Thus, aromatic aldehydes can be selectively reduced in the presence of aliphatic aldehydes and ketones, which remain intact. Under the same reaction conditions, aromatic ketones react sufficiently slowly, so that selective reduction of aromatic aldehydes can be achieved in presence of a ketone. Carboxylic acids, esters and amides are not reduced.

2. Results and discussion

2.1. Thermochemical considerations

Heterogeneous catalytic hydrogenation of benzaldehyde to benzyl alcohol using a Pd/C catalyst should proceed through initial adsorption of both the aldehyde (H-acceptor) and a source

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of hydrogen (H-donor) onto the catalyst surface. This step is followed by hydrogen transfer from the H-donor to the aldehyde. The reaction possibly proceeds through formation of an intermediate Pd(H) species, although there is evidence that H-transfer takes place directly from the adsorbed H-donor to the adsorbed H-acceptor, without formation of a real Pd(H) species [7]. Eqs. (1)–(3) can be used to assess the exo- or endothermicity of reactions leading to reduction of benzaldehyde to benzyl alcohol.

$$\mathrm{PhCHO} + 2\mathrm{PdH} \leftrightarrows \mathrm{PhCH_2OH} + 2\mathrm{Pd} \tag{1}$$

$$\mathrm{PhCHO} + \mathrm{H_3PO_2} + \mathrm{H_2O} \leftrightarrows \mathrm{PhCH_2OH} + \mathrm{H_3PO_3} \tag{2}$$

$$\mathrm{PhCH_2OH} + \mathrm{O_2} \leftrightarrows \mathrm{PhCHO} + [\mathrm{H_2O_2}] \tag{3}$$

Reaction (1) describes the formation of Pd(H) species on the catalyst surface. Reaction (2) describes the overall enthalpy change in the reduction of benzaldehyde by phosphinic acid, whereas reaction (3) is introduced because of evidence (see below) that oxygen can easily reverse the reduction even in the presence of a phosphinate H-donor.

Using the various enthalpies of formation [8,9], the enthalpy change of reaction (ΔH_R) for the process (1) was estimated to be $-42\,\mathrm{kJ\,mol^{-1}}$ [10]. This low value suggests that both the forward and reverse reaction might proceed spontaneously, depending on the reaction entropy. The low exothermicity is not too surprising given the wealth of evidence for the reversibility of many hydrogenation/dehydrogenation reactions involving carbonyl and alcohol groups. For example, the Oppenauer reaction proceeds through reduction of a carbonyl group with simultaneous oxidation of an alcohol, with or without catalysis [11]. Homogeneous catalytic reduction of aldehydes and ketones can be achieved with a variety of H-donors based on alcohols, such as 2-propanol [5].

The exothermicity is $-150\,\mathrm{kJ\,mol^{-1}}$ for the reaction (2), which considers only the total enthalpy of the process without the intervention of PdH species [12]. This value is rather large to allow easy back reaction. However, if the back reaction (2) were assisted by oxygen, as seems likely from the evidence given below, the endothermicity of process (2) would be replaced by the alternative return path of process (3), which is exothermic by $-114\,\mathrm{kJ\,mol^{-1}}$ [11]. This value is still slightly lower than that of the forward reaction (2). Thus, while it is not easy to drive back the reaction (2) directly, there is sufficient energy gain in the alternative reaction (3) for benzyl alcohol to be reoxidised into benzaldehyde in the presence of air. The enthalpies of reactions (1)–(3) suggest that reduction of benzaldehyde to benzyl alcohol is reversible in the presence of oxygen, whether or not PdH is an intermediate species. The actual rates of reactions (1)–(3) will be governed by the respective free energies of activation, and also by the surface densities of H-acceptor, H-donor and oxygen at the catalyst surface. These surface densities are in turn governed by the respective adsorption constants and by the relative concentrations of H-acceptor, H-donor and oxygen in solution. The solubility of oxygen (air) is known to be low in most solvents [13], while the adsorption constants (K) for aldehydes are unknown. These constants can be calculated from the adsorption isotherms, as described below.

3. Measurement of the adsorption isotherms

The importance of adsorption isotherms in gas-phase catalysis is well recognised, and their measurement has become a standard procedure for examining gas-phase processes occurring on solid surfaces [14]. In sharp contrast, measurement of adsorption isotherms for liquid-phase reactions with heterogeneous catalysts is much less advanced. This relative lack of interest probably reflects the difficulties presented by attempting to incorporate the effects of solvent. Using a new approach to measuring adsorption isotherms in the liquid phase, it has been possible to gain some practical understanding of the interplay of solvents and solutes in reactivity at a heterogeneous catalyst surface [1,15,16]. For example, it has been demonstrated that the hydrogenation rate at the surface of heterogeneous catalyst in THF can be made to vary from zero to a maximum and then back to zero again, simply by changing the proportion of water in THF [1]. This new approach to measurement and usage of isotherms in heterogeneous catalysis has been preferentially tested on commercially available catalysts rather than on idealised surfaces frequently used in the gas-phase research.

The competition for sites on a heterogeneous catalyst surface by an H-donor and an H-acceptor has been discussed extensively [1,15,16]. For example, it has been shown that the adsorption constant for a common H-donor, sodium phosphinate, onto the surface of a palladium catalyst from solution is about 20 times larger than that of a typical H-acceptor, thus, the substance to be reduced is easily displaced from the catalyst surface by the substance supplying the hydrogen [16]. Obviously, no reduction can take place if the surface of a heterogeneous catalyst is covered by the H-donor molecules and no H-acceptor molecules can reach it. Thus, it is necessary to decrease the competition from the H-donor and/or to increase the competition from the H-acceptor to enable an H-acceptor to populate the catalyst surface to a reasonable extent in the presence of a strongly adsorbing H-donor. There are two obvious ways to change the surface densities of the two substances, as the H-donor and H-acceptor are both present in the solvent surrounding the catalyst. The first is to change their relative adsorption constants by changing the solvent. The second is to reduce the concentration of the H-donor and simultaneously increase the concentration of the H-acceptor by manipulation of a mixed solvent system [17]. One of the ways to adjust the surface densities is to use a mixture of largely immiscible solvents, such as water and toluene. The concentration of water-soluble H-donor (e.g., sodium formate or sodium phosphinate) in this biphasic solvent system is high in the aqueous phase but very low in the organic phase. In contrast, the solubility of a typical H-acceptor, such as benzaldehyde, is high in the organic phase (toluene) and low in the aqueous phase. The Pd/C catalyst is strongly hydrophobic so that even with rapid stirring of a biphasic toluene/water system, the catalyst stays in the organic phase. Thus, the Pd/C catalyst is surrounded by a high concentration of the H-acceptor in the toluene phase but by only a low concentration of the

H-donor, because most of the latter remains in the aqueous phase.

As an alternative to the biphasic solvent system, a monophasic mixture of solvents can be used if the solvents are mutually soluble, as happens with water and THF. Addition of an inorganic H-donor, such as solid sodium phosphinate, to such a monophasic system will result in some of the sodium phosphinate dissolving, the amount being critically controlled by the proportion of water in the THF. Thus, the concentration of the H-donor can be maintained at a constant low level by adjusting the proportion of water in the THF solvent. Similar to the biphasic solvent discussed above, this monophasic arrangement results in a high concentration of the H-acceptor and a low concentration of the H-donor surrounding a heterogeneous catalyst. In turn, this adjustment of the effective solution concentration gives more appropriate surface densities of the H-acceptor and the H-donor at the surface of the heterogeneous catalyst.

Whereas manipulation of the surface density of the H-donor in relation to the H-acceptor on the catalyst surface can be achieved by the use of mono- or biphasic mixtures of water with an organic solvent, the ability of the H-acceptor to compete with the solvent itself for the surface sites is also important. Clearly, the stronger the adsorption of the H-acceptor onto the catalyst surface, the better it can compete for sites against the H-donor [16]. Thus, choice of the organic solvent component becomes important not only due to its effect in adjusting the surface densities but also in its effect on the actual strength of adsorption of the H-acceptor onto the surface of the catalyst. If the solvent itself adsorbs too strongly, it displaces the H-acceptor, whereby both H-acceptor and H-donor surface densities become low, which slows down or even stops the reduction. The effects of solvent on adsorption of an H-acceptor can be investigated by measuring adsorption isotherms for the acceptor on a catalyst surface in a variety of solvents or in mixtures of solvents [1,15,16].

In the present work, isotherms were measured for adsorption of benzaldehyde onto the surface of a Pd/C catalyst in a range of solvents (Fig. 1). Each isotherm was determined by using different weights of catalyst and then measuring the uptake of benzaldehyde from solution in any chosen solvent. The adsorption constants (*K*) were calculated from the resulting plots [15,16]. By varying the solvent or varying the composition of mixed solvents, the changes in the strength of adsorption of benzaldehyde onto the catalyst surface could be examined quantitatively.

The estimated adsorption coefficients ($K \times 10^2$ mg) for benzaldehyde in the three solvents (DCM, THF and ethanol) are 0.04, 3.2 and 42.6, respectively. Their relative values (1:810:1080) indicate how well benzaldehyde can compete with the respective solvent for sites on the catalyst surface and how widely this competitive ability varies. For example, DCM competes strongly with benzaldehyde for sites on the catalyst surface. In contrast, ethanol competes so poorly that benzaldehyde almost excludes the solvent from the surface of the catalyst. Therefore, benzaldehyde in ethanol adsorbs 1080 times as efficiently to the catalyst surface as it does when dissolved in DCM. THF holds an intermediate position. Thus, for benzaldehyde to adsorb onto the surface of the catalyst at sufficient concentration to enable rapid reaction, a solvent, such as THF, is preferable to DCM. The hydrophilic ethanol is not a good choice because although it allows easy adsorption of aldehyde onto the catalyst, it also allows a high concentration of the strongly adsorbing sodium phosphinate H-donor, which is soluble in ethanol and has an adsorption coefficient some 20 times larger than that of benzaldehyde [16].

As a second example, the adsorption coefficients ($K \times 10^2$ mg) for 9-anthraldehyde (Fig. 2) in four separate solvents (DCM, THF, ethyl acetate and toluene) were found to be 0.32, 0.30, 0.05 and 0.02, respectively (relative values = 16:15:2.5:1). The adsorption of this multi-ring aromatic compound onto the catalyst surface is relatively weak from all solvents. There is not much to choose between DCM or THF, which allow the strongest adsorption of 9-anthraldehyde, and toluene or ethyl acetate that provide the weakest.

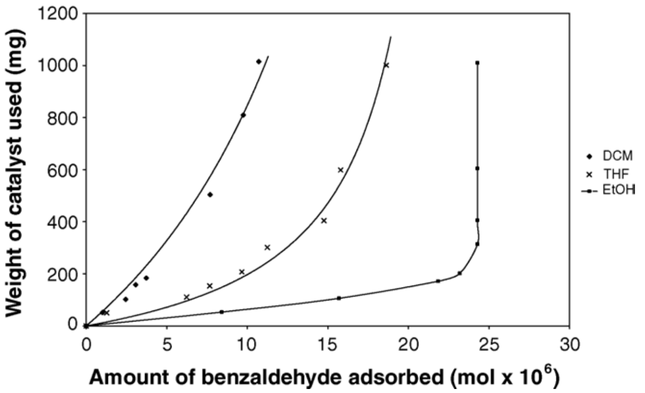

Fig. 1. Plots showing the adsorption of benzaldehyde from dichloromethane, THF and ethanol using the following amounts of benzaldehyde: 2.71×10^{-5} mol (DCM), 2.34×10^{-5} mol (THF) and 2.43×10^{-5} mol (ethanol). Actual adsorptions ($s' \times 10^6$ mol) for different amounts of Pd/C catalyst (mg; ordinate) are plotted on the abscissa. Calculated adsorption constants (*K*, mg) are 0.0004 (DCM), 0.0075 (THF) and 0.4255 (ethanol).

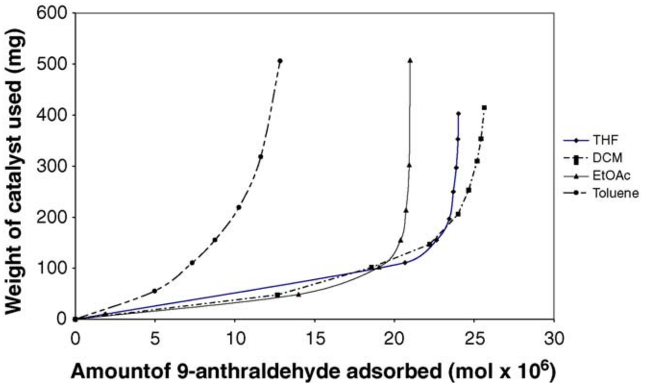

Fig. 2. Plots showing the adsorption of 9-anthraldehyde from dicloromethane, toluene, ethyl acetate and THF solutions at 20 °C. Initial solutions (*s*) are each of 20 mL and contained the following amounts of 9-anthraldehyde: 1.144×10^{-5} mol (toluene), 1.68×10^{-5} mol (ethyl acetate), 2.46×10^{-5} mol (THF) and 2.62×10^{-5} mol (dicloromethane). Actual adsorptions ($s' \times 10^6$ mol) for different amounts of Pd/C catalyst (mg; ordinate) are plotted on the abscissa. The calculated adsorption constants (*K*, mg) for the three solvents are 0.0229 (toluene), 0.0502 (ethyl acetate) and 0.2992 (THF).

Considering the adsorption coefficients for benzaldehyde and 9-anthraldehyde in various solvents, it appears that THF might be the most convenient solvent for reduction of aldehydes because of its boiling point, general stability and complete miscibility with water.

By adjusting the amount of water mixed with THF, an optimum solubility for the intended H-donor (sodium phosphinate) could be found experimentally, as described below. However, hydrogenolyses of other functional groups in toluene/water systems had been shown to be highly successful [2,15]. Therefore, as the role of solvent was under special scrutiny in the present work, we decided to quantitatively compare the reduction of aromatic aldehydes in a biphasic toluene/water system with the same reduction in a monophasic THF/water mixture, chosen based on the isotherm measurements. As described below, major practical differences were found between the two solvent systems in reduction of aromatic aldehydes.

4. Transfer reduction of benzaldehyde

We used a single large batch of a commercially available Pd/C catalyst in all of the following experiments so as to avoid variations in behaviour between batches. All the reaction mixtures were stirred rapidly. The catalyst remained suspended in the organic layer in both the biphasic toluene/water and monophasic THF/water systems. Approximate rates of reduction of benzaldehyde to benzyl alcohol were measured by monitoring the amounts of the two during reaction by GC, after calibrating the GC responses with authentic samples of starting material and product.

4.1. In biphasic toluene/water systems

At first, attempts were made to reduce benzaldehyde in refluxing toluene/water (azeotrope, bp 90 °C) with slightly more than an equimolar amount of sodium phosphinate in the presence of the catalyst. Some initial formation of benzyl alcohol was observed but this soon ceased, after which the amount of alcohol began to decrease with time, while the amount of benzaldehyde began to rise towards its initial level. More sodium phosphinate was added in stages until it was in large excess, because this effect could result from insufficient concentration of the H-donor at the catalyst surface. This approach led to very slow but complete reduction to benzyl alcohol. Because the concentration of H-donor appeared to be so important, another reduction of benzaldehyde with a large initial excess of sodium phosphinate was left to proceed without addition of more H-donor during the reaction. In this case, the initially fast reaction slowed down, with the formation of benzyl alcohol ceasing at ca. 50% of the aldehyde conversion. The reaction then appeared to reverse itself because the yield of benzyl alcohol began to fall and the amount of benzaldehyde to increase. Note that the combined amounts of benzaldehyde and benzyl alcohol remained almost constant and neither was transformed into other products. This result indicated that the reaction (1) or (2) proceeded from left to right, but as the H-donor concentration decreased, benzyl alcohol began to be oxidised back to benzaldehyde, possibly through oxidation by dissolved oxygen (reaction (3)).

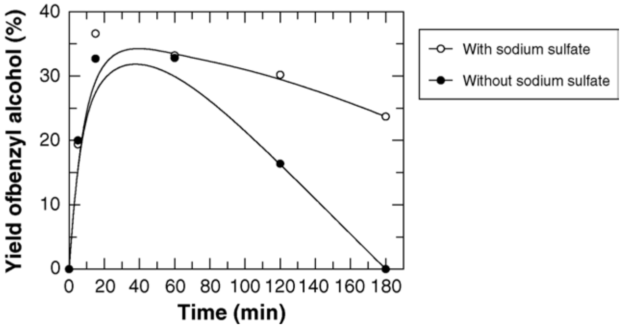

Fig. 3. Plots showing the percentage yield of benzyl alcohol formed by reduction of benzaldehyde against the time of reaction in the absence of sodium sulphate and in the presence of 2 M sodium sulphate. Other reaction conditions for this toluene/water system are given in Section 8.

Under most oxidative conditions, benzaldehyde is known to be oxidised to benzoic acid easier than benzyl alcohol can be oxidised to benzaldehyde [18]. It seems clear that in the *presence* of some H-donor, oxidation of benzyl alcohol to benzaldehyde stops at the aldehyde stage. No attempt was made to exclude air from the system in these experiments, thus, it is likely that oxygen acts as an alternative H-acceptor so as to reverse the reduction, as shown in reaction (3).

4.1.1. The effect of oxygen on the reversibility of reaction (1)

By excluding oxygen from the system (reaction done under argon), the above reduction of benzaldehyde could be driven to completion without any back oxidation of the alcohol. Oxygen as a hydrogen acceptor is probably reduced initially to superoxide or more likely to peroxide under the reaction conditions used in this work [19]. However, any peroxide would be readily reduced to water by sodium phosphinate and would thus be unavailable to oxidise benzaldehyde to benzoic acid.

To examine the effect of changes in oxygen concentration on the reduction of benzaldehyde in a more quantitative manner, an inert inorganic salt was added to the reaction medium. It is known that addition of salts, such as sodium sulphate or potassium chloride, reduces the equilibrium concentration of oxygen in solution [20]. Accordingly, in a separate experiment, sodium sulphate (2 M) was included with the sodium phosphinate in the aqueous solution. The solubility of oxygen in an aqueous solution of sodium sulphate of this strength is 1.42 mL/L, compared with 5.78 mL/L in pure water, thus, the oxygen concentration is reduced by 4.1 times on addition of inert sodium sulphate [19]. Intentionally, in this experiment, we used sodium phosphinate sufficient to reduce only half of the available benzaldehyde so that the reverse oxidation could be readily observed. The rate of reduction to benzyl alcohol was monitored by GC (Fig. 3). It is seen that formation of benzyl alcohol reaches a maximum at about 20–25 min but then begins to decrease markedly. The experiment was repeated without addition of sodium sulphate (Fig. 3). The initial rate of formation of benzyl alcohol over the first 15–20 min of reaction was mostly unaffected by sodium sulphate. Thus, with regard to the reduction stage, addition of sodium sulphate had almost no effect on the rate. However, starting from the point when the yield of benzyl alcohol began to decrease as it began to be oxidised back to benzaldehyde (25–30 min), the reoxidation rate was reduced by a factor of 4 in the presence of sodium sulphate. Given the lower solubility of oxygen in aqueous 2 M sodium sulphate solutions, the difference in rates of oxidation of benzyl alcohol can be attributed to the change in concentration of dissolved oxygen. Thus, for the toluene/water system at 90 °C, it is clear that aerial oxygen can slow down and even reverse the reduction of benzaldehyde unless the concentration of sodium phosphinate remains high or the concentration of dissolved oxygen is reduced.

4.1.2. *Transfer reduction of other aromatic aldehydes in toluene/water*

Despite the high concentrations of the H-donor needed in the above reduction of benzaldehyde, it seemed useful to examine the general applicability of the method to other aromatic aldehydes (Table 1). It is immediately clear from the table that in the biphasic toluene/water system, the yields of alcohols from reduction of aldehydes are generally inferior to those from reduction of benzaldehyde itself. No attempt was made to optimise the reaction conditions in order to obtain better yields, because two other problems were manifest. First, particularly for multi-ring aromatic compounds, some decarbonylation of the starting aldehyde was observed. Second, in some cases, there was significant over-reduction of the initially formed primary alcohol to give the corresponding methyl group (e.g., see the last three entries in Table 1). In view of the far better results obtained on changing to the monophasic THF/water system, the reduction of aromatic aldehydes in the biphasic toluene/water system was not investigated any further.

Table 1
Reduction of various aromatic aldehydes (RCHO) to the corresponding alcohols (RCH_2OH)[a]

Carboxaldehyde (RCHO, R=)	Conversion (%)	Yield (%)
Phenyl	97	89
4-Fluorophenyl	92	91
3-Chlorophenyl	46	35[b]
4-Chlorophenyl	51	40[b]
3-Methoxyphenyl	62	61
4-Methoxyphenyl	65	61
3,4-Dimethoxyphenyl	41	32
4-(α,α,α)Trifluoromethylphenyl	38	32
3,4-Methylenedioxyphenyl	45	36
2-Thiophenyl	5	2
2-Quinolinyl	96	34[c]
4-Quinolinyl	96	45[d]
2-Naphthyl	79	6[e]
9-Anthranyl	90	25[f]
9-Phenanthryl	100	50[g]

[a] All the reactions were carried out for the same times (see Section 8). There was no attempt to optimise the conversions or yields.

[b] A very small quantity (<1%) of benzyl alcohol was formed by dechlorination.

[c] 1,2,3,4-Tetrahydroquinoline-2-methanol and 1,2,3,4-tetrahydroquinoline were formed in 51 and 4% uncorrected yields, respectively. The reduced products were separated by GC and identified by mass spectral analysis.

[d] 1,2,3,4-Tetrahydroquinoline-4-methanol and 4-methylquinoline were formed in 8 and 41% uncorrected yields, respectively. The reduced products were separated by GC and identified by mass spectral analysis.

[e] 2-Methylnaphalene was formed in 61% yield. Percentage yield was determined using an internal standard and corrected for detector response.

[f] 9-Methylanthracene, anthracene and 9,10-dihydroanthracene were formed in respective yields of 33, 13 and 2%. 9-Methylanthracene and anthracene percentage yield were determined by GC after 60 min reaction using an internal standard and corrected for detector response. 9,10-Dihydroanthracene was identified by mass spectral analysis and the yield was determined by GC and was uncorrected.

[g] 9-Methylphenanthrene was formed in 49% yield. Percentage yield was determined using an internal standard and corrected for detector response.

4.2. *In monophasic THF/water system*

The adsorption isotherms described above indicate that aldehydes should be able to compete with sodium phosphinate more efficiently for sites on the catalyst surface in THF than in toluene. At the same time, the concentration of sodium phosphinate can be controlled by adjusting the proportion of water in the monophasic THF/water system. By comparing the rates of reduction of benzaldehyde as the proportion of water in THF was varied, it was found that a mixture of 80% THF to 20% water (v/v) produced the fastest reaction at room temperature (about 20 °C). This ratio of THF to water was adopted for all the other reductions carried out in this survey (Table 3).

An increase in rate on changing from anhydrous THF to the 80:20 THF/water mixture agrees well with earlier work, which showed that rates of hydrogenolysis of phenolic ethers could be varied from zero to a maximum and back to zero simply by changing the proportions of THF and water [1]. The use of THF/water rather than toluene/water gave very fast reduction of all the investigated aromatic aldehydes to alcohols in high yields at room temperature. Importantly, decarbonylation and over-reduction of the product alcohol to methyl group became almost non-existent.

The method of reduction in THF/water is very easy to use, requiring no expensive reagents. Further, it is not necessary to exclude air from the system because the reduction rate is so high that the reverse oxidation of benzyl alcohol cannot compete with it. The product alcohols are easily separated from the catalyst by filtration, while inorganic oxidation products, such as sodium phosphate, are readily removed by washing the product with water. Advantageously, after filtration from the product, the Pd/C catalyst could be rinsed with hot THF and re-used in subsequent reductions. This simple recovery process was repeated five times, without any apparent loss in catalytic activity towards reduction of aromatic aldehydes.

5. Selectivity for reduction of aromatic aldehydes in the presence of other carbonyl-containing compounds

Although the THF/water system provides for easy reduction of an aromatic aldehyde to the respective alcohol, for the reaction to be really useful, it should preferably be selective as well. This sort of selectivity can be difficult to achieve with metal hydrides. For example, sodium tetrahydroborate easily reduces both aliphatic and aromatic aldehydes and ketones but not carboxylic esters [5,6]. In marked contrast, in the THF/water system with sodium phosphinate and Pd/C catalyst, aliphatic aldehydes and ketones, and all carboxylic acids, esters and amides remain unaffected by this reductive procedure (Table 5). Importantly, aromatic ketones are either not reduced at all or react only slowly. For example, when a mixture of benzaldehyde and acetophenone was subjected to the THF/water reduction, benzyl alcohol was formed in 92% yield in 5 min, together with just 3.5% of 1-phenylethanol. This compares well with a 96% yield of benzyl alcohol obtained in the same time in the absence of acetophenone. If the reaction was left on for an extended time after all of the benzaldehyde had been reduced and more sodium phosphinate was added, acetophenone was then reduced slowly to 1-phenylethanol. Thus, the reduction of aromatic aldehydes is indeed highly selective. The reaction proceeds at room temperature, being fast, high-yielding and requiring no special reaction conditions. The use of THF is industrially acceptable for these reactions, because no peroxides of THF can build up under the reducing conditions.

6. The effect of a strong donor molecule on reduction rates

The rationalization of reduction rates of aldehydes in terms of differential adsorption of H-donor and H-acceptor on the catalyst surface suggests that any other strongly adsorbing species that is present might be expected to limit the reduction. Strong electron donors should prevent H-acceptor and/or H-donor molecules from adsorbing by competing for available sites on the catalyst surface. Triphenylphosphine is known to be a good, neutral electron donor, which is soluble in organic solvents but not in water. Indeed, when triphenylphosphine was added to a reduction of benzaldehyde with sodium phosphinate and Pd/C in either toluene/water or in THF/water, the rate of reduction fell to very low levels. For example, when triphenylphosphine was added so that it was approximately equimolar with benzaldehyde in the THF/water system, only about 10% of benzyl alcohol was formed in 15 min, compared with the usual 96% in 5 min. In effect, triphenylphosphine acts as a heterogeneous palladium catalyst poison in contrast to its usual role in *homogeneous* catalysis, where it acts as a valuable ligand for enhancing the activity of palladium or its salts [5].

7. Conclusion

The overall rate of heterogeneous catalytic transfer hydrogenation of aromatic aldehydes results from a competition of an H-acceptor with an H-donor and solvent for sites on the catalyst surface. In molar terms, the concentration of solvent is necessarily in large excess compared with the H-acceptor and H-donor solutes and should remain in excess if reagents and products are to remain in solution. However, by competing for sites at the catalyst surface, the actual solvent used can have a profound effect on the reaction rate.

In any one solvent system, an ability to adjust the relative concentrations of H-donor and H-acceptor at the catalyst surface is important because the H-donor is generally much more strongly adsorbed than the H-acceptor. In effect, by acting as a “poison” similar to triphenylphosphine, the strongly adsorbing H-donor prevents the more weakly adsorbing H-acceptor from settling on the surface of the catalyst. In monophasic THF/water systems, the concentration of H-donor at the catalyst surface can be reduced by limiting its concentration in the organic phase. This control can be most easily achieved by adjusting the proportion of water in the monophasic THF/water solvent or by relying on the low solubility of the donor in the upper organic phase of a biphasic toluene/water system.

Thus, from two points of view, the choice of solvent for heterogeneous transfer reduction becomes important for attaining maximum efficiency of reduction. The choice is made easier by measuring adsorption isotherms for H-donor and H-acceptor in a small range of solvents. Then, by use of the most suitable solvent, reduction of aromatic aldehydes to the corresponding primary alcohols by sodium phosphinate and Pd/C catalyst was changed from a relatively slow, modest-yielding reaction at 90 °C in toluene/water into a very rapid, high-yielding, selective, room temperature reduction in THF/water.

Oxygen in air was found to play an important role in acting as an apparent inhibitor to reduction. This inhibition is actually a dehydrogenation of the product primary alcohol back to the original aldehyde. The ensuing inhibition arises from a balance of the desired forward reduction and a simultaneous back oxidation, which is almost as fast. The rate of reduction is so high in THF/water under the best conditions presently described that the reverse oxidation cannot compete.

8. Experimental

Compounds were characterized and assessed for purity by combinations of melting point, mass spectrometry, proton magnetic resonance spectroscopy, infrared spectroscopy and elemental analysis. Mass spectra and GC/MS data were recorded at 70 eV on a Trio 1000 Quadrupole or on a VG 7070E double-focusing instrument.

^{1}H NMR spectra were recorded on either a Bruker ACE200 at 200 MHz or a Varian Gemini instrument at 300 MHz with tetramethylsilane as internal standard and $CDCl_3$ as solvent. UV spectra were measured on either a Hewlett Packard diode array or a Shimadzu UV-260 spectrometer. IR spectra were obtained on a Perkin-Elmer 883 double beam instrument, liquids as films and solids as Nujol mulls. Gas chromatography was carried out on a Dani 3800 or a Phillips PU 4600 instrument, using FFAP, SE-30 or Carbowax capillary columns. Thin layer chromatography was done on silica gel $60F_{250}$ plates (Merck). C, H, N analyses were obtained on a Carlo Erba 1106 elemental analyser.

In all the experiments, the catalyst was 10% (w/w) palladium-on-carbon (PdC) taken from a single batch of catalyst supplied by Johnson–Matthey. The specific metal area was $26\,m^2\,g^{-1}$.

8.1. Measurement of isotherms for aldehydes adsorbing onto Pd/C catalyst in various solvents

All isotherms were measured at 20 °C. The amounts of solute adsorbed from solution onto the catalyst were determined by

UV spectroscopy at a selected wavelength, after first measuring the extinction coefficient (ε) from solutions of known concentrations. In a typical isotherm measurement, a solution of benzaldehyde (29 mg; 0.275×10^{-3} mol) in DCM (250 mL) was prepared (solution A; concentration, $s = 1.1 \times 10^{-3}$ M). Eight samples of catalyst were weighed out accurately (c_w; approximately 50, 100, 150, 200, 300, 400, 600 and 1000 mg). The 25 mL of solution A was added to each sample. An additional sample of solution A was used as a blank. The mixtures of catalyst and solution A were stirred gently so as not to disrupt the physical structure of the catalyst and its support. After 15 min, stirring was stopped and samples were left to stand for 10 min to allow the catalyst to settle out. From each solution, several millilitres were withdrawn using a syringe fitted with a fine filter (Whatman mountable filter; PTFE; 13 mm; 0.2 μm pore size) and UV absorption was measured at 280 nm to give the new solution concentration (s''). The amount of benzaldehyde s' that had adsorbed onto the catalyst was calculated from the difference in UV absorption between the sample and the blank. A graph was drawn with c_w as ordinate and $s' = s - s''$ as abscissa (Fig. 1). From the initial linear portion of the graph, for which $c_w = a \times s'$, the constant a (the weight of catalyst saturated per mole of benzaldehyde adsorbed) was obtained. Then, a second graph was prepared with $c_w = a \times s'$ as ordinate and $s'/(s - s')$ as abscissa, using points from the curved portion of the first graph. The second graph was linear with slope = $1/K$, where K is the adsorption constant for benzaldehyde in DCM. The experiment was repeated for other solvents to give a range of K values (see the text). More details and data appear in earlier publications [1,15,16].

8.2. Transfer reduction of aromatic aldehydes in toluene/water solvent system

In a typical experiment, a solution of sodium phosphinate (NaH_2PO_2; 3 g, 3.4×10^{-2} mol) in water (10 mL) was added dropwise over 3 min to a rapidly stirred mixture of benzaldehyde (1.03 g, 9.7×10^{-3} mol) in toluene (20 mL) and Pd/C catalyst (0.1 g) at 90 °C. The yield of benzyl alcohol reached 97% after 120 min.

All other aldehydes listed in Table 1 were reduced similarly in the yields stated after a standard reaction time of 120 min. Where unknown peaks appeared in addition to starting aldehyde and product alcohol (as with 9-anthraldehyde), the new substances were identified by GC/MS and column chromatography and then by comparison with authentic samples. These extra reduction products are listed in Table 1.

8.3. Transfer reduction of ketones in toluene/water

In a typical experiment, a solution of benzophenone (0.12 g; 6.48×10^{-4} mol) in toluene (10 mL) was heated to 90 °C with Pd/C catalyst (0.11 g) and a solution of sodium phosphinate (0.15 g; 1.7×10^{-3} mol) in water (5 mL). After 60 min, 65% of the benzophenone had been converted to diphenylmethanol (benzhydrol; 25% yield) and diphenylmethane (39% yield). Other aromatic ketones were examined similarly and are listed with their product yields in Table 2.

Table 2
Conversion of ketones (R^1R^2CO) into the corresponding alcohols (R^1R^2CHOH) and methylenes ($R^1R^2CH_2$) in tolunene/water[a]

Ketone	Conversion (%)	Yield of alcohol (%)	Yield of methylene (%)[b]
Benzophenone	65	25	39
4-Methoxybenzophenone	64	7	54
Acetophenone	80	23	54
Propiophenone	74	11	49

[a] Reaction conditions were the same as for the aldehydes (Table 1). No attempt was made to optimise yields.
[b] Methylene were formed by over-reduction of the alcohols.

Aliphatic aldehydes (octanal and dodecanal) and ketones (3-nonanone and 2-octanone) remained completely unaffected in these reduction conditions.

8.4. Transfer reduction of benzaldehyde in the presence of sodium sulphate

A solution of benzaldehyde (1.01 g; 9.54×10^{-3} mol) in toluene (20 mL) was heated to 90 °C with Pd/C catalyst (0.10 g) and a solution of sodium phosphinate (0.36 g; 4.1×10^{-3} mol) in water (10 mL), which had been saturated with $Na_2SO_4 \cdot H_2O$ (3 g). In a separate experiment, the reaction was repeated but without any added sodium sulphate. The yields of benzyl alcohol with time are shown in Fig. 3. The total of the molar amounts of benzaldehyde and benzyl alcohol remained constant throughout the reaction.

8.5. Determination of percentage yields of products and percentage conversions of starting materials

The extent of reaction was monitored at regular intervals for each of the reductions described below. Aliquots (100 μL) were removed from the upper organic layer of the reaction mixture and the amounts of starting material and products were measured from GC peak areas. To assist quantification, an inert internal standard, dodecane (0.10 g), was added to every reaction mixture at the start. Also for the purposes of quantification, the relative response factors of benzaldehydes, benzyl alcohols and dodecane were determined separately by analysing their mixtures at known concentrations. Finally, the GC yields were checked by work-up of larger scale reaction mixtures and isolation of products in the usual way for several aldehydes.

8.6. Preparation of authentic samples of primary alcohols

All aldehydes were purchased (Aldrich) but many of their reduction products, the primary alcohols (Tables 1 and 2), were not available. These alcohols were needed for purposes of identification and quantification and were synthesised separately. In a typical reaction, 2-thiophenecarboxaldehyde (0.49 g, 4.4×10^{-3} mol) in methanol (10 mL) was reacted with sodium tetrahydroborate (0.09 g; 2.3×10^{-3} mol) at room temperature for 2 h. Water (10 mL) was added to stop the reaction and the products were extracted into DCM (3×10 mL). The combined organic phases were dried (Na_2SO_4) and the solvent was evaporated to give the required 2-(hydroxymethyl)thiophene, ^{1}H 4.93 (2H, s), 7.29 (1H, m), 7.55 (1H, m), 8.12 (1H, m); MS, m/z 170 (M^+). Most of the ^{1}H NMR spectra for the primary alcohols listed in Tables 1 and 2 are known [21].

8.7. *Optimum solvent ratio for the reduction of benzaldehyde in THF/water solvent systems*

A series of reductions was carried out to establish the best conditions for using THF/water mixtures as a monophasic solvent system. The proportion of water was changed so that the total solvent volume remained at 10 mL (THF:water = x:$10 - x$ mL). Typically, benzaldehyde (0.514 g; 4.85×10^{-4} mol) in THF (9 mL) and sodium phosphinate (0.17 g; 1.93×10^{-3} mol) in water (1 mL) were mixed and stirred. Pd/C catalyst (0.106 g) was added at time zero and the reaction was stopped after 5 min. The yield of benzyl alcohol was measured by GC. Similar experiments were carried out for $x = 10$, 9, 8, 7, 6 and 5 mL. The amounts of benzyl alcohol produced were (% yield (x ratio)): 0 (10), 30 (9), 96 (8), 90 (7), 91 (6) and 89 (5).

8.8. *General method for transfer reduction of aromatic aldehydes in the THF/water solvent system*

In a typical experiment, a solution of sodium phosphinate (NaH_2PO_2; 0.173 g; 1.97×10^{-3} mol) in water (2 mL) was added all at once to rapidly stirred mixture of benzaldehyde (0.065 g; 6.14×10^{-4} mol) in THF (8 mL) and Pd/C catalyst (0.1 g) at 20 °C. A few aliquots (100 μL) were removed from the solution at intervals to monitor the course of reduction, with the reaction stopped after 5 min. The yield of benzyl alcohol was 96%.

All the other aldehydes listed in Table 3 were similarly reduced to the corresponding primary alcohols in the yields stated after the standard reaction time of 5 min. For 9-anthraldehyde, the reported reaction components were separated by column chromatography on silica gel (DCM as eluent) prior to identification (Table 3).

8.9. *Transfer reduction of aromatic ketones and aliphatic ketones in the THF/water solvent system*

Acetophenone (0.09 g; 7.45×10^{-4} mol) in THF (8 mL) was stirred with Pd/C catalyst (0.11 g) and sodium phosphinate (0.19 g; 2.19×10^{-3} mol) in water (2 mL) at room temperature for 5 min. Work-up in the usual way showed that 1-phenylethanol had been formed in 33% yield. Benzophenone, 4-methoxybenzophenone and propiophenone were examined similarly (Table 4).

No reduction of aliphatic aldehydes (octanal or dodecanal) or ketones (3-nonanone or 2-octanone) was observed in the same reaction conditions.

Table 3
Reduction of aromatic aldehydes (RCHO) to the corresponding alcohols (RCH_2OH) in THF/water[a]

Aromatic aldehyde (RCHO, R=)	Conversion (%)	Yield by GC (%)[a]	Yield by isolation (%)[a]
Phenyl	100	100	97
4-Fluorophenyl	97	85	90
3-Chlorophenyl	89	66[b]	
4-Chlorophenyl	93	83[c]	89
3-Methoxyphenyl	100	81[c]	90
4-Methoxyphenyl	100	78[c]	
3,4-Dimethoxyphenyl	98	87[d]	82
4-(α,α,α)Trifluorophenyl	100	91[d]	
3,4-Methylenedioxyphenyl	99	94	
2-Thiophenyl	64	55	
2-Pyridyl	100	67	
3-Pyridyl	86	52	
4-Pyridyl	99	66	
2-Quinolinyl	100	30[e]	
4-Quinolinyl	89	34[f]	
2-Naphthyl	87	76	
9-Anthryl	75	33[g]	21
9-Phenanthryl	75	32[h]	

[a] All reaction were carried out for the same times. Conversion and yields are not optimised.

[b] Benzyl alcohol (from hydrogenolysis of chlorine) and toluene were also formed in 18 and 3% yield, respectively.

[c] Benzyl alcohol (from hydrogenolysis of chlorine) and toluene were also formed in 5 and 2% yield, respectively.

[d] Very small amounts (1–7%) of the corresponding methylene compounds (RCH_3) were formed by over-reduction.

[e] 2-Methylquinoline and quinoline were formed in respective yields of 7 and 2% yield, respectively. The yields were uncorrected.

[f] A precipitate appears after isolation. It was dissolved in ethanol and GC/MS revealed to be a mixture of 4-methylquinoline, quinoline and 4-quinolinemethanol.

[g] 9-Methylanthracene and 9,10-dihydroanthracene were formed in yields of 17 and 5% yield, respectively.

[h] 9-Methylphenanthrene was formed in 43% yield (uncorrected).

In a separate experiment, a solution of sodium phosphinate (0.07 g; 6.6×10^{-4} mol) in water (2 mL) was added to a stirred mixture of benzaldehyde (0.061 g; 5.7×10^{-4} mol), acetophenone (0.076 g; 6.3×10^{-4} mol) and Pd/C catalyst (0.1 g) in THF (8 mL) at room temperature. After 5 min, the yields of benzyl alcohol and 1-phenylethanol were 92 and 3.5%, respectively (Table 5).

Table 4
Conversion of ketones (R^1R^2CO) into the corresponding alcohols (R^1R^2CHOH) and methylenes ($R^1R^2CHCH_2$) in THF/water[a]

Ketone	Conversion (%)	Yield of alcohol (%)	Yield of methylene (%)
Benzophenone	34	4	25
4-Methoxybenzophenone	35	7	19
Acetophenone	40	33	–
Propiophenone	37	25	–

[a] Reaction conditions were the same as for the aldehydes (Table 3). No attempt was made to optimise yields. Conversions and yields of alcohols were determined by GC after 5 min reaction, using an internal standard for quantification. Percentages yields of methylenes were determined by GC using an internal standard and was uncorrected for detector response.

Table 5
Selective reduction of carbonyl compounds in THF/water using sodium phosphinate as hydrogen donor and Pd/C (10%, w/w) as a catalyst[a]

Ketone	Product (s)	Yield (%)[b]
Benzaldehyde	Benzyl alcohol	96.2
Benzaldehyde	Benzyl alcohol	92.0
Acetophenone	1-Phenylethanol	3.5
Benzaldehyde	Benzyl alcohol	98.6
Octaldehyde	–[c]	–[c]
Benzaldehyde	Benzyl alcohol	92.0
2-Octanone	–[c]	–[c]

[a] The reaction was run at room temperature using approximately 6×10^{-4} mol of each substrate, dodecane (internal standard, 0.30 g), Pd/C catalyst (10%, w/w; 0.1 g), sodium phosphinate (0.07 g, 6.6×10^{-4} mol) in THF/water (8:2 mL).

[b] The products yields were determined by GC after 5 min of reaction, using the internal standard for quantification.

[c] There was no conversation of the starting material.

8.10. Transfer reduction of benzaldehyde with added triphenylphosphine

Benzaldehyde (0.44 g; 4.15×10^{-3} mol) and triphenylphosphine (1.27 g; 4.84×10^{-3} mol) in toluene (10 mL) were stirred together with Pd/C catalyst (0.15 g) at 90 °C. A solution of sodium phosphinate (0.15 g; 1.7×10^{-2} mol) in water (5 mL) was added to this mixture dropwise over 3 min. After 60 min, only 4% of benzyl alcohol was formed. Similarly, benzaldehyde (0.05 g; 4.92×10^{-4} mol) and triphenylphosphine (1.405 g; 5.35×10^{-4} mol) in THF (8 mL) were stirred at 20 °C with Pd/C catalyst (0.1 g) and sodium phosphinate (0.17 g; 1.93×10^{-3} mol) in water (2 mL). After 60 min, only 8% of benzyl alcohol was formed.

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