Metal-Assisted Reactions. Part XXX.* Control of Rates of Heterogeneously Catalyzed Transfer Hydrogenolysis through Changes in Solvent Composition

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Adsorption isotherms in the liquid phase can be used to determine the relative strengths of adsorption of reactants and solvent at a catalyst surface. Such isotherms can then be used to indicate which type of solvent would be most suitable for a heterogeneously catalyzed reaction in the liquid-phase. Solubility in any chosen solvent is also important. As examples, rates of heterogeneously catalyzed liquid-phase transfer hydrogenolyzes of aryl tetrazolyl ethers (1) have been shown to be highly dependent on both the nature of the solvent and on the solution concentrations of the reactants. The rate of reaction can be varied from zero to a maximum and then back to zero simply by adjusting the solubility of the reductant through changes in the proportion of water in a mixed-solvent system.

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Introduction

Understanding the basis of heterogeneous catalysis in the gas phase is of considerable economic importance to largescale chemistry and is examined widely, being supported by a galaxy of instrumental techniques.^[1] In contrast, fundamental theoretical and experimental approaches to the economically more important heterogeneous catalysis of a multitude of much smaller-scale reactions in the liquid phase receive far less attention, possibly because of the extra difficulties introduced by solvents in an already complex area of research.^[2] For heterogeneous catalysis in the liquid phase, the solvent can influence rates of reaction through solvation of reactants and intermediates in solution, but it can also affect the rate by competing with reactant molecules for active sites on the surface of a heterogeneous catalyst. Solvent may also stabilize or destabilize transition states or intermediates formed on the catalyst surface. The competition for surface sites can be selective in that the effect of solvent on reactant (A) is unlikely to be same as its effect on reactant (B). When a combination of solvents is used, their effects on binding of the two reactants become more complex.

The temperature range available for liquid-phase reactions is usually much more restricted than it is for gas-phase chemistry, for which even modest catalysts at near ambient temperatures can become important if the reaction temperature is increased sufficiently. Large increases in temperature are not generally a serious option for most liquid-phase chemistry, particularly when chirality or the integrity of other functional groups must be conserved. For a catalyzed reaction to proceed at a reasonable rate in the liquid phase it needs to be efficient at temperatures in a restricted range of about $0-150^{\circ}$ C. For the reasons just outlined, even small changes in the type and composition of a solvent system can have a significant impact on the efficiency of a catalyzed liquidphase process. Accordingly, an ability to enhance catalytic activity at modest temperatures in the liquid phase by simply altering the composition of a solvent system can be of crucial importance.

To help fill the gap in fundamental knowledge concerning heterogeneously catalyzed liquid-phase processes, results available from homogeneous catalytic liquid-phase chemistry are frequently transferred conceptually to notionally corresponding heterogeneous reactions, mostly through intuition rather than through any fundamental conviction of the 'fitness' of such applications. Solvation effects in solution are unlikely to be helpful in describing solvent effects at the surface of a heterogeneous catalyst.

In one particular area, the heterogeneous catalysis of liquid-phase reduction, there has been some consideration of the importance and influence of solvent on reactivity.^[2] It has been shown that rates of heterogeneous hydrogenolysis of aryl ethers may be controlled by use of biphasic systems.^[3] It is also clear that, in aqueous/organic solvent biphasic systems,

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even the hydrophobicity or hydrophilicity of the heterogeneous catalyst is very important in improving or impeding reactivity.^[4]

In the present work, the influence of solvent composition on rates of heterogeneous catalytic transfer hydrogenolysis has been examined. The approach is aimed at real working catalysts and commercially available catalysts have been used in the present work rather than idealized single-crystal surfaces.

Results and Discussion

Hydrogenolysis of Aryl Tetrazolyl Ethers to Arenes

Phenols can be converted easily into aryl tetrazolyl ethers (1), which in turn are easily hydrogenolyzed to an arene (2) through use of a hydrogen donor and Pd/C catalyst (Scheme 1). This reaction provides a simple rapid means for *ipso* replacement of a phenolic OH by H.^[5]

The influence of the heterocyclic part of these ethers on C–O bond strength has been revealed through X-ray studies.^[6] On the basis of these results, it has been possible to extend Scheme 1 to the hydrogenolysis of similar pseudosaccharyl ethers^[7] and to devise a novel cross-coupling reaction with organometallic reagents, in which a phenolic C–O bond is replaced by a C–C bond (C-alkyl or C-aryl).^[8] In the present work, the role of solvent composition on the rate of hydrogenolysis (Scheme 1) is examined. For convenience, 5-(2-naphthoxy)-1*H*-tetrazole (1a) was chosen for hydrogenolysis because the rate of formation of the naphthalene product of this high yielding, rapid reaction is easily monitored by gas chromatography. Water-soluble sodium phosphinate was used as the hydrogen donor.

Isotherms for Adsorption of Aryl Ethers (1) onto a Pd/C Catalyst Surface

To gain some understanding of the role of solvent, a new type of 'Langmuir' isotherm has been used to measure the relative strengths of adsorption of a variety of organic compounds onto commercial catalysts from a range of solvents.^[9–11] Some typical isotherms are shown in Figure 1 for ether (1a). The ability of ethers (1) to adsorb onto the Pd metal of a 10% Pd/C catalyst surface is strongly dependent on the solvent. For example, in ethanol, adsorption of ether (1a) is sufficiently strong that it almost entirely prevents co-adsorption of solvent onto the catalytic metal but, for toluene, the solvent competes significantly with the ether for sites on the metal surface. The behaviour of tetrahydrofuran (THF) lies between those of toluene and ethanol (Fig. 1). Solvents clearly play an important role in the degree of adsorption of reactants from solution onto a catalyst surface.



Fig. 1. Typical adsorption isotherms for ether (1a) adsorbing onto a Pd/C (10% w/w) catalyst having a specific metal area of $26 \text{ m}^2 \text{ g}^{-1}$. Solutions (L, M, N; 20×10^{-6} M) of ether (1a) were prepared for each of the solvents toluene (L), THF (M), and ethanol (N). In a typical experiment, an amount of catalyst (*x* mg) was weighed out and stirred with an aliquot of solution L for 15–20 min. The catalyst was filtered off and the amount of ether (1a) remaining in solution was determined by UV/visible absorption measurements. The quantity of catalyst was varied between 0 < x < 1000 mg. Finally, the amount of ether (1a) adsorbed on the catalyst was plotted against the weight of catalyst used. The determinations were repeated for solutions M and N, giving the three isotherms shown.

The observed relative binding efficiencies of solvent and reactants, as measured by binding constants K,^[9–11] suggested that it might be possible to change the rate of hydrogenolysis (Scheme 1) in a predictable manner by manipulation of the type of solvent and also by regulation of the solubilities of reactants through changes in solvent composition. This reaction is one in which reactant A (the naphthyl ether (1a)) and reactant B (the hydrogen donor, sodium phosphinate) compete for sites on the catalyst surface before hydrogen is transferred to complete the hydrogenolysis. The reaction is known to be one in which H₂ gas is not formed but rather one in which H is transferred from reactant (B) to (A) on the catalyst metal surface.^[12]

In a first set of experiments, a monophasic mixed solvent system was used and consisted of THF containing water, the water content varying from 0 to 50% (v/v). The ether (1a) was soluble in all cases. The hydrogen donor, sodium phosphinate, is not soluble in THF but, as more water is added to the solvent system, its solubility increases. By changing its solubility, it is then possible to alter the amount of phophinate that can adsorb onto the catalyst surface so that the phosphinate then competes increasingly with ether (1a) for a limited number of sites on the catalyst surface. For each change in the THF/H₂O composition, the initial rate of formation of naphthalene was measured.



In a second set of experiments, the solvent composition remained constant (benzene/ethanol/water). Ether (1a) is soluble in this system but sodium phosphinate is only sparingly soluble. In successive experiments, the solubility of the sodium phosphinate was increased by the addition of aliquots of [18]crown-6, a phase-transfer agent that is known to solubilize sodium salts into organic solvents. Thus, as more crown ether was added, more phosphinate appeared in the monophasic mixed solvent system and was able to compete with ether (1a) for sites on the catalyst surface. Again, the rate of formation of naphthalene was monitored for each addition of crown ether. The results of these experiments are described below.

Expected Variation in the Rate of Hydrogenolysis (Scheme 1) with Variation in the Coverage of the Catalyst Surface by Two Reactants

For two substances A and B reacting at the surface of a catalyst, the rate of formation of product P can be written as in Equation (1), in which k' is a general rate constant and θ_A and θ_B represent fractional equilibrium coverages of the catalyst metal surface by A and B, respectively. (In a heterogeneous reaction, the rate constant k' is also dependent on the quantity of catalyst used.)

$$\frac{\mathrm{dP}}{\mathrm{d}t} = k' \times \theta_{\mathrm{A}} \times \theta_{\mathrm{B}} \tag{1}$$

In the equilibria shown in Scheme 2, K_A and K_B are binding constants measuring the respective adsorptions of each reactant onto the surface of a catalyst C, with CA* and CB* representing the adsorbed complexes of the reactants on the catalyst metal surface.

The concentrations of A and B in solution are s_A and s_B , respectively, and s'_A and s'_B represent the amounts of A and B adsorbed from solution onto the catalyst. The two binding constants give Equations (2*a*) and (2*b*) from which may be obtained the ratio, K_A/K_B or θ_A/θ_B (Equations (3*a*) and (3*b*)).

$$K_{\rm A} = \frac{\theta_{\rm A}}{(1 - \theta_{\rm A} - \theta_{\rm B})(s_{\rm A} - s_{\rm A}')} \tag{2a}$$

$$K_{\rm B} = \frac{\theta_{\rm B}}{(1 - \theta_{\rm A} - \theta_{\rm B})(s_{\rm B} - s_{\rm B}')} \tag{2b}$$

0

$$\frac{K_{\rm A}}{K_{\rm B}} = \frac{\theta_{\rm A}}{\theta_{\rm B}} \times \frac{(s_{\rm B} - s_{\rm B}')}{(s_{\rm A} - s_{\rm A}')} \quad \text{or} \tag{3a}$$

$$\frac{\theta_{\rm A}}{\theta_{\rm B}} = \frac{K_{\rm A}}{K_{\rm B}} \times \frac{(s_{\rm A} - s_{\rm A}')}{(s_{\rm B} - s_{\rm B}')} \tag{3b}$$

For complete coverage of the catalyst surface (highly likely in a real system in solution for which the concentrations of solutes are high), $\theta_A + \theta_B = 1$. Thus, by rearrangement of the Equations (3a) and (3b), Equation (4) for θ_B is obtained. A similar expression may be obtained for θ_A .

$$\theta_{\rm B} = \frac{K_{\rm B}(s_{\rm B} - s_{\rm B}')}{K_{\rm B}(s_{\rm B} - s_{\rm B}') + K_{\rm A}(s_{\rm A} - s_{\rm A}')} \tag{4}$$

Usually, in solution during most of any reaction, $s_A \gg s'_A$ and $s_B \gg s'_B$, and this leads to new expressions for θ_A and θ_B , in which $K = K_A/K_B$ (Equations (5*a*) and (5*b*)).

$$\theta_{\rm A} = \frac{K s_{\rm A}}{s_{\rm B} + K s_{\rm A}} \tag{5a}$$

$$\theta_{\rm B} = \frac{Ks_{\rm B}}{s_{\rm A} + Ks_{\rm A}} \tag{5b}$$

If r (= dP/dt) is the rate of reaction, the rate can be estimated from Equation (1) after substituting for θ_A and θ_B from Equations (5*a*) and (5*b*), as in Equation (6).

$$r = \frac{k'Ks_{\rm A}s_{\rm B}}{(s_{\rm B} + Ks_{\rm A})^2} \tag{6}$$

By differentiation of Equation (6) with respect to either s_A or s_B , it is found that the maximum rate (r_{max}) is obtained when $Ks_A = s_B$ so that the maximum rate of reaction on the catalyst surface is given by $r_{max} = k'/4$.

The equations show that, for θ_A or $\theta_B = 0$, the rate of reaction becomes zero, as expected, but reaches a maximum at k'/4, when $Ks_A = s_B$. The last relationship implies that, for maximum rate of reaction, the reactants should cover equal fractions of the catalyst surface. However, the fractions are themselves controlled by both the concentrations of the two reactants in solution (s_A and s_B) and their relative binding strengths ($K = K_A/K_B$). Thus, if $K_A \gg K_B$ or $K_B \gg K_A$, then the solution strengths (s_A and s_B) of A or B need to be adjusted if θ_A is to be about equal to θ_B .

Equations (2)–(6) reveal the importance of relative binding strengths and of the type of solvent used in these heterogeneous reactions. Binding strength depends on solvent and on the catalyst surface. It is a measure of how well one reactant can compete with other reactants or with solvents for sites on the catalyst surface. For example, with a strongly binding component B in solution above a catalyst surface (both $K_{\rm B}$ and $s_{\rm B}$ large), then $s_{\rm B} \gg K s_{\rm A}$, thus reactant A would be excluded from the catalyst surface. In such circumstances, no reaction should be observed. If the amount of B in solution is reduced to such a level that s_B is approximately equal to Ks_A , then reactant A will adsorb onto the catalyst surface to about the same extent as B and allow the reaction to proceed. When $s_B \ll K s_A$, reactant B will be excluded from the surface and the reaction rate will fall to zero again. It can be seen that in situations in which both reactants bind to a catalyst surface with similar binding energies, the rate of reaction will then be critically dependent on solution concentrations of A and B and also on the nature of the solvent. As described below, the rate of hydrogenolysis (Scheme 1)

could be maximized by ensuring that sodium phosphinate, an anion known to bind strongly to palladium, [9-11] could not reach a sufficiently high solution concentration that it could exclude ether (1a) from the catalyst surface. For these exper-

iments, the concentration of A (ether (1a)) was kept constant and the concentration of B (sodium phosphinate) in solution was varied, either by changing a mixed solvent composition or by use of a phase-transfer catalyst.

The rate constant k' includes the amount of catalyst used and, therefore, for a situation in which $\theta_A = \theta_B$, the maximum rate increases if more catalyst is used (assuming temperature and pressure to be constant).

Rate of Formation of Naphthalene as the Composition of THF/H₂O Mixtures is Varied

In this series of experiments, hydrogenolysis of ether (1a) was carried out in a monophasic aqueous tetrahydrofuran system, in which the percentage of water was varied from 0 to 50% (v/v). Initial rates of formation of naphthalene were monitored by gas chromatographic analysis of aliquots of the reactant solution. Normally, at about 60–80°C, this hydrogenolysis can be completed in about 10–20 min.^[5] In the complete absence of water, with THF, no naphthalene was formed. With some added water, hydrogenolysis was found to proceed slowly. As more water was included in the monophasic solvent system, the rate of formation of naphthalene increased to a maximum of 2.24×10^{-7} mol⁻¹ s⁻¹ when there was added, the rate of hydrogenolysis began to decrease until, with 50% of added water, it had ceased entirely.

Reference to the equations in the section above explains this behaviour. With no water present in the THF, there can be no significant dissolution of sodium phosphinate and, therefore, it can not be adsorbed onto the catalyst surface, which is covered by ether (1a) and solvent. No reduction can be expected and none was observed. As the proportion of water is increased, the concentration of sodium phosphinate in the solvent system increases and so too does its adsorption onto the surface of the catalyst. The observed increase in rate of hydrogenolysis with increasing water content of the solvent system reflects the increasing coverage of the catalyst surface by sodium phosphinate. The fractional coverages (θ_A and $\theta_{\rm B}$) of the catalyst surface by ether (1a) and sodium phosphinate change as the hydrogen donor becomes more soluble. With both the ether substrate and the hydrogen donor present together on the catalyst surface, hydrogenolysis proceeds and reaches a maximum when the relative coverages of ether and hydrogen donor are about equal. Because the hydrogen donor has a much greater binding constant than does ether (1a) in THF/water,^[9-11] it is to be expected that as the hydrogen donor concentration in solution increases, it will displace more and more ether (1a) from the surface of the catalyst. In these circumstances, the reaction rate begins to fall and eventually reaches zero when all ether (1a) has been excluded from the catalyst surface. With the quantities of catalyst and the solution strengths used here, a maximum rate was observed at a THF/water ratio of about 70: 30 (v/v). At a composition of 50: 50, hydrogenolysis (Scheme 1) would not even start, even though all components were in solution. These experimental results are entirely in keeping with previous observations^[13] on the importance of donor concentration on reaction rate. The rate variations in THF/water illustrate the importance of solvent composition in controlling heterogeneously catalyzed reactions through control of the relative proportions of two reactants on the surface of a catalyst.

Rate of Formation of Naphthalene as the Concentration of Hydrogen Donor in Solution is Varied

In a second set of experiments, the concentration of hydrogen donor, again in a monophasic solvent system, was adjusted through use of a phase-transfer agent. Ether (1a) was dissolved in an organic phase consisting of the upper layer from the azeotropic mixture of benzene/ethanol/water (86.0: 12.7: 1.3, v/v/v).^[12] Pd/C catalyst was added, together with solid sodium phosphinate, and the mixture was refluxed; most of the sodium phosphinate remained undissolved. At the low concentration of hydrogen donor, formation of naphthalene was slow (20% yield in 30 min) compared with the normal biphasic solvent conditions (complete reaction in 10 min).^[10] In a separate experiment, addition of [18]crown-6 at a 0.1 molar ratio to the hydrogen donor caused a large increase in the rate of formation of naphthalene, a 40% yield being produced in 30 min and 80% in 4 h. For further experiments, it was expected that addition of even more [18]crown-6 should again increase the concentration of hydrogen donor and lead to another increase in the rate of formation of naphthalene. However, at a 0.4 molar ratio of crown ether to hydrogen donor, the rate of reaction fell significantly and, after 4 h, only about 45% of naphthalene had been formed. Addition of more phase-transfer catalyst led to a further fall in the rate of hydrogenolysis. These results are consistent with those described for the THF/H2O experiment and with others reported earlier.^[3] Increasing the concentration of sodium phosphinate in solution for the heterogeneously catalyzed hydrogenolysis reaction (Scheme 1) leads to increasing exclusion of the ether from the catalyst surface and eventually to a reduction in reaction rate or even complete cessation of reaction. This behaviour is quite unlike solution chemistry, for which continuously increasing the concentrations of reactants in solution generally leads to a continuous increase in reaction rate.

Hydrophobicity or Hydrophilicity of the Heterogeneous Catalyst

As shown above, adjustment of solvent composition can have a marked effect on the rate of hydrogenolysis through control of the relative coverages of the catalyst surface by the reactants. In those experiments, the mixed solvents formed a monophasic system with the catalyst dispersed in it. Inorganic, water-soluble hydrogen donors are not normally soluble in organic solvents. In a *biphasic* water/organic solvent system (for example, benzene or toluene/water), the concentration of the substance to be reduced (e.g. ether (1a)) is high in the organic layer and low in the aqueous layer. Conversely, the hydrogen donor concentration (e.g. sodium phosphinate) is high in the aqueous layer and low in the organic layer. Since the amounts of substrate and donor adsorbed onto the catalyst surface depend on both binding constants and concentrations, the environment surrounding the catalyst becomes important. Pd/C catalyst is hydrophobic. Even with vigorous stirring, it remains suspended in the organic hydrophobic layer of a water/benzene system and not the aqueous. The hydrogen donor is dissolved almost entirely in the aqueous phase and the substance to be reduced is dissolved in the organic phase. Because the catalyst lies in the organic phase, access to its surface by the substance to be reduced is unimpeded but, for the hydrogen donor, access is restricted since there is little of the hydrogen donor in the organic layer. Effectively, access to the catalyst is controlled by having two slightly miscible solvents, with each of the reactants in a different phase and the catalyst favouring one phase over the other.

To demonstrate the effect of changing environment on catalyst behaviour, ether (1a) was dissolved in the upper phase of a typical biphasic mixture of benzene or toluene, ethanol, and water and was treated with sodium phosphinate in the presence of Pd/C catalyst at 65°C. Hydrogenolysis proceeded normally.^[13] After about 5 min when some 57% yield of naphthalene had been produced, stirring was stopped and, immediately, a sonicator was switched on so as to effect greater mixing of the phases. After less than 2 min, sonication had produced a 'one-phase' emulsified system of the organic solvent and water, with the catalyst finely dispersed throughout it.^[14a] Sonication was stopped and heating at 65°C was continued but no further formation of naphthalene occurred. The emulsion remained stable overnight (18 h) and still no more naphthalene was formed during this period. This abrupt cessation of catalytic activity upon sonication of a heterogeneously catalyzed reaction is in contrast to the usual finding that sonication is generally beneficial for many catalytic processes, even hydrogenation.[14b] Although deleterious changes in the nature and activity of a heterogeneous catalyst have been noted during extended sonication, the complete cessation of reaction observed here was virtually instantaneous on starting sonication. It is unlikely in so short a time that the catalyst could have been so damaged as to no longer act catalytically. The result is explicable in terms of a greatly increased access of the strongly binding hydrogen donor to the catalyst surface through rapid emulsification and dispersal of the catalyst into a thoroughly mixed benzene/ethanol/water emulsion phase. Such a situation allows easy access of the hydrogen donor to the catalyst surface.

Conclusions

Adsorption isotherms were used to assess relative binding strengths of hydrogen-acceptor and hydrogen-donor reactants to the catalyst surface in different solvents. For the heterogeneously catalyzed reaction in the liquid phase using a water-soluble hydrogen donor, access of the reactants to the catalyst surface can be controlled through selection of the solvent system. This choice is made so as to obtain favourable binding of the reactants to the surface and, at the same time,

to regulate the effective concentration of the hydrogen donor at the catalyst surface by adjusting its solubility in solution. In one set of experiments with ether (1a), the latter was dissolved in a monophasic aqueous/organic solvent mixture. By adjusting the proportion of water present, it was possible to control the amount of hydrogen donor dissolved in the solvent. The catalyst (Pd/C) remained suspended in the organic layer. As more water was added, the solubility of the sodium phosphinate hydrogen donor in the organic layer increased, leading first to an increase in the rate of reaction and then to a cessation. The control of rate was such that, with either no water or a lot of water in the organic layer hydrogenolysis ceased, but with intermediate amounts the rate of hydrogenolysis passed through a maximum. Other experiments designed to control adsorption of the sodium phosphinate onto the catalyst surface through changes in solvent and access of reactants to the catalyst surface have led to similar conclusions. Rates of heterogeneously catalyzed hydrogenolysis of ethers (1) can be changed easily from zero to a maximum by simple variations of the solvent system.

Experimental

Sodium phosphinate and THF were purchased (Aldrich). The supply of sodium phosphinate was refreshed regularly and its purity was checked by titration with ceric sulfate/ferrous ammonium sulfate.^[15] 5-(2-Naphthoxy)-1*H*-phenyltetrazole was prepared by a literature method.^[6] Generally, the 10% Pd/C catalyst was a fresh standard commercial sample, having a metal dispersion area of about $26 \text{ m}^2 \text{ g}^{-1}$ (Johnson Matthey). For consistency, all experiments were carried out on the same batch of catalyst, except for the sonication experiment, for which a different 10% Pd/C catalyst was used (Engelhardt). Gas chromatographic monitoring was carried out on a Dani instrument, using an FFAP capillary column and dodecane as internal standard.

Adsorption Isotherms

These were determined for the ether (1a) and for phosphinate by the method briefly described in Figure 1. Greater detail can be found in earlier publications.^[9–11]

Hydrogenolysis of 5-(2-Naphthoxy)-IH-phenyltetrazole (THF, with Increasing Proportions of Water)

In a typical experiment, the catalyst (10% Pd/C, 100 mg; Johnson Matthey) and sodium phosphinate (15 mg, 0.17 mmol) were added to a solution of the ether (1a) (50 mg, 0.17 mmol) and dodecane (50 μ L) in THF (10 mL), to which had been added *x* (mL) of water (in the different experiments, *x* varied from 0 to 10). The mixture was vigorously stirred and heated under reflux (65°C). The formation of naphthalene was monitored by analysing aliquots withdrawn at intervals. Initial reaction rates were determined (to about 20% of reaction). The maximum observed initial rate in the series was 2.24×10^{-7} mol s⁻¹. No attempt was made to find the true maximum. For the case of *x* = 0 and of *x* = 10, no formation of naphthalene was observed over a period of 45 min and starting material was recovered. For the case of *x* = 0, even though no reaction had been observed under reflux over a period of 45 min, it could be made to proceed normally to give naphthalene simply by the addition of some water (2–3 mL).

Hydrogenolysis of 5-(2-Naphthoxy)-IH-phenyltetrazole (1a) in a Benzene/Ethanol/Water Azeotrope, with Increasing Amounts of Added [18]Crown-6

The solvent was the upper organic phase $(74.1 : 18.5 : 7.4 v/v/v; bp 65^{\circ}C)$ obtained by azeotroping a mixture of benzene, ethanol, and water.^[13] The hydrogen donor used in these experiments was not significantly soluble in this organic phase. In a typical experiment, a stirred solution of

5-(2-naphthoxy)-1*H*-phenyltetrazole (44.3 mg, 1.54×10^{-4} mol) and durene (15.4 mg, internal as chromatography standard) in the azeotrope (40 mL), containing Pd/C catalyst (10% w/w, 25.2 mg) and sodium phosphinate (42.6 mg, 4.8×10^{-4} mol), was refluxed and aliquots of the reaction mixture (ca. 0.1 mL) were taken at intervals to measure the formation of naphthalene. Experiments were performed with and without [18]crown-6, used as a phase-transfer catalyst to increase the solubility of the sodium phosphinate. The amount of crown ether ranged from 0 to 8.1 mg (4.5×10^{-5} mol) to 32 mg (1.78×10^{-4} mol).

Sonic Irradiation of the Hydrogenolysis Reaction

To a solution of ether (1a) (200 mg, 0.7 mmol) in a two-phase mixture of benzene/ethanol/water (7 : 3 : 2; 25 mL),^[16] containing sodium phosphinate (220 mg, 2.5 mmol) was added Pd/C catalyst (10%, 200 mg; Engelhard). The mixture was stirred while being heated under gentle reflux. The formation of naphthalene was monitored by gas chromatography after removing aliquots of the upper phase. After 5 min, the yield of naphthalene reached about 57%. At this stage, the solution was sonicated at 20 kHz, using a piezoelectric horn having a titanium extension which projected into the reaction medium and delivered about 20 W cm⁻². Within less than 2 min, the mixture had completely emulsified, the catalyst becoming uniformly distrubuted throughout the liquid. Sonication was stopped and, with continued heating under gentle reflux, the formation of naphthalene was monitored for a further 18 h. There was no observable increase in the amount of naphthalene that had been formed before sonication had started.

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