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Nickel bromide as a hydrogen transfer catalyst

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Catalysed transfer hydrogenation of a range of organics is achieved using $NiBr_2$ in alkaline $^{i}PrOH$

During our studies on $NiX_2(PPh_{3-n}py_n)_2$ complexes (X = halogen, py = 2-pyridyl, n = 1–3), some of which are water-soluble,[1] a report appeared on the use of a $NiCl_2(PPh_3)_2$–NaOH–$^{i}PrOH$ system for transfer hydrogenation of ketones and aldehydes.[2] Our Ni(II) pyridylphosphines, under corresponding conditions, were of comparable activity, but some 'blank tests' soon revealed that $NiCl_2{\cdot}6H_2O$ had similar activity, while anhydrous $NiBr_2$ or $NiI_2{\cdot}6H_2O$ had much higher activity. For example, 90% conversion of cyclohexanone to cyclohexanol was attained after 1 h of refluxing in an alkaline $^{i}PrOH$ solution containing $NiBr_2$, whereas conversions of only 14 and 24%, respectively, were achieved with $NiCl_2(PPh_3)_2$ and $NiBr_2(PPh_3)_2$, under comparable conditions (0.4 mM Ni, 35 mM NaOH, 100 mM ketone in 3.0 cm^3 $^{i}PrOH$). More optimised reaction conditions for a practical scale synthesis (5 mM $NiBr_2$, 0.5 M NaOH, 1.5 M cyclohexanone) resulted in 100% conversion after 30 min refluxing. The use of $CoBr_2$ and CoI_2 under corresponding conditions resulted in conversions of ~60%. The simplicity of the system using commercially available $NiBr_2$ makes it attractive for laboratory hydrogenations without the need for H_2, especially as it is applicable to a wide range of organic substrates (see below). A further advantage is that the system operates under aerobic conditions, while the often used platinum metal, phosphine-containing complexes are usually air-sensitive in solution.[3]

$$\text{substrate (A)} + {}^{i}\text{PrOH} \xrightarrow[\text{reflux}]{\text{NiBr}_2,\ \text{NaOH}} \text{A(H)}_2 + \text{acetone} \qquad (1)$$

The $NiBr_2$–NaOH–$^{i}PrOH$ system† (eqn. 1) can be effective for catalytic hydrogen transfer of saturated ketones, aldehydes, alk-1-enes, cyclohex-2-en-1-one, nitrobenzene and 4-nitrobenzaldehyde (Table 1). For cyclohexanone, butan-2-one and oct-1-ene, the conversion activity is generally comparable with, or greater than, that reported by others for transfer hydrogenation using more 'exotic' catalysts.[2–6] The extremely efficient hydrogenation of a terminal olefin such as oct-1-ene using $^{i}PrOH$ is unusual; more commonly, 'hydrogenated aromatics' like 1,2-dihydronaphthalene and indoline have been used as hydrogen donors with either homogeneous or heterogeneous-based platinum metal systems,[6] but the systems are much less efficient than the $NiBr_2$ system. Internal olefins and cod are not hydrogenated; of note, the system effects selective hydrogenation of oct-1-ene in a 1 : 1 mixture with (*t*) oct-2-ene, but at a lower rate (27% conversion in 0.5 h) than with oct-1-ene alone. With α,β-unsaturated ketones, cyclohex-2-en-1-one is converted initially to cyclohexanone but this saturated ketone is subsequently reduced at a rate comparable to the rate of appearance of the cyclohexanol; *e.g.* after 0.5 h, there is 40% reduction of the enone to equal amounts of the saturated ketone and alcohol, while after 48 h there is 73% conversion of enone to essentially just cyclohexanol (Table 1)—no cyclohexen-1-ol is detected. The non-reduction of but-3-en-2-one may be due to its coordination to the Ni as a chelate, which could block coordination of the propoxide (the usually postulated steps for a homogeneously catalysed process are: propoxide coordination, hydride abstraction, and transfer to coordinated substrate[3,7]). Nitrobenzene is reduced selectively to aniline, but the conversion is only ~20% after 48 h, and there is a significant 'base-only' contribution (Table 1); correspondingly, 4-nitrobenzaldehyde undergoes Ni-promoted hydrogenation (38% in 24 h), but non-selectively to mainly the nitrobenzyl alcohol and smaller amounts of aminobenzyl alcohol and the aminobenzaldehyde.

Of interest, although the use of base co-catalysts for metal complex catalysed hydrogen transfer is common,[2–4,7–11] data on the 'base-only' systems are rarely reported.[8,9] In the strongly basic medium employed in our work, acetophenone and heptan-1-al are effectively reduced to the respective alcohols even in the absence of the $NiBr_2$ (Table 1). The basic conditions used preclude reduction of pentane-2,4-dione and hexane-2,5-dione because these were converted, respectively, to sodium acetylacetonate and a self-condensation product (probably 5-methylundec-5-ene-2,7,10-trione); in a related manner, benzaldehyde undergoes the Cannizzaro reaction to yield the alcohol and sodium benzoate. Nitriles were not reduced and, to our knowledge, there are no reports on transfer hydrogenation of nitriles.

The $NiBr_2$ system appears to be homogeneous, at least for cyclohexanone. For all the substrate systems, the initially light-coloured solutions gradually darken through yellow to orange with reaction time but, after filtration through a 0.22 μm pore, the orange filtrate showed no loss of activity, for example, for

Table 1 $NiBr_2$ catalysed transfer hydrogenation of organics[a]

Substrate	% Conversion (time, h)	% Conversion (time, h)[b]	Product(s)
Cyclohexanone	99.9 (0.5)	29.1 (0.5)	Cyclohexanol
Acetophenone	60.1 (4), 99.4 (24)	65.4 (4), 98.8 (24)	1-Phenylethanol
Butan-2-one	55.2 (2), 97.2 (24)	8.4 (2), 18.5 (24)	Butan-2-ol
Pentan-2-one	31.0 (24), 99.9 (48)	12.2 (24), 27.8 (48)	Pentan-2-ol
Oct-1-ene	99.9 (0.5)	0.0 (0.5)	*n*-Octane
Cyclohex-2-en-1-one	73.0 (48)[c]	20.0 (48)[d]	Cyclohexanone Cyclohexanol
Heptan-1-al	92.2 (4)	83.0 (4)	Heptan-1-ol
Nitrobenzene	14.1 (0.5), 19.2 (48)	4.0 (0.5), 14.0 (48)	Aniline
4-Nitrobenzaldehyde	38.0 (24)[e]	12.5 (24)[f]	ABA, NBA, AB[e]

[a] In 24 h, no conversion for: (*t*) oct-2-ene, but-3-en-2-one, pentane-2,4-dione, hexane-2,5-dione, 2-propionic acid, MeCN, PhCN and benzene, and < 5% for cyclooctene and cod. [b] In presence of base only, no $NiBr_2$. [c] 2% ketone, 71% alcohol. [d] 4% ketone, 16% alcohol. [e] 10.5% 4-aminobenzyl alcohol (ABA), 21.9% 4-nitrobenzyl alcohol (NBA), 5.6% 4-aminobenzaldehyde (AB). [f] 3.6% ABA, 7.4% NBA, 1.5% AB.

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cyclohexanone hydrogenation; also the addition of Hg(0), an inhibitor for colloidal activity,[12] to a 'fresh' system gave only a 7% decrease in conversion (*cf.* Table 1). Further, the solid inorganic residue obtained after a hydrogenation of cyclohexanone was re-used three more times for repeat conversions, when only slow deactivation of the catalyst was noted: 1st run, 99.9% conversion after 0.5 h; 2nd, 95% (3 h); 3rd, 92% (7 h); 4th, 63% (3 h).

Of interest, addition of up to 4 equiv. of PPh_3 to the $NiBr_2$ system has no effect on the rate of hydrogenation of cyclohexanone, and also $NiBr_2(PPh_3)_2$ is unstable in the alkaline medium (with dissociation of the phosphine), implying that in the earlier work on the $NiCl_2(PPh_3)_2$ system[2] the precursor catalyst may be simply $NiCl_2$.

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Notes and references

† A glass vessel (35 mL) equipped with a Teflon-coated magnetic stirrer was charged in air with $NiBr_2$, NaOH and ^{i}PrOH, and the mixture heated at 95 °C to yield a pale-green solution. After this was cooled to rt, the vessel was fitted with a condenser and charged with substrate; the mixture was then refluxed, and samples were withdrawn for GC and NMR analysis (Table 1). The $NiBr_2$: NaOH : substrate ratios were 1 : 85 : 250 in all cases, with [$NiBr_2$] between 1–6 mM.

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