Unprecedented efficient hydrogenation of arenes in biphasic liquid–liquid catalysis by re-usable aqueous colloidal suspensions of rhodium

Jürgen Schulz, Alain Roucoux* and Henri Patin

Laboratoire de Chimie Organique et des Substances Naturelles, CNRS ESA 6052 Ecole Nationale Superieure de Chimie de Rennes, Avenue du Gal Leclerc, 35700 Rennes, France. E-mail: Alain.Roucoux@ensc-rennes.fr

Received (in Cambridge, UK) 19th January 1999, Accepted 18th February 1999

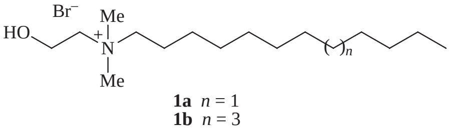
A reduced aqueous colloidal suspension of rhodium shows efficient activity for the catalytic hydrogenation of various benzene derivatives under biphasic conditions at room temperature and under atmospheric hydrogen pressure; the aqueous phase containing the Rh(0) particles can be re-used for further runs with a complete conservation of activity.

Among catalytic processes, hydrogenation of arenes is of great interest, in particular with the increasing industrial demand for low-aromatic diesel fuels[1] and the conversion of benzene to cyclohexane which still represents the most important industrial hydrogenation reaction.[2] Generally, the catalytic transformation is carried out with heterogeneous catalysts.[3] Recently some pure homogeneous[4] or microheterogeneous[5] systems under drastic conditions (pressure and/or high temperature) have been reported for hydrogenation of arenes.

Biphasic systems consisting of a water-phase containing catalytic species and a non-miscible organic phase continue to attract interest for economic and ecological reasons. In most cases, water-soluble homogeneous catalysts containing hydrophilic phosphines are widely used.[6] An original approach is to use colloidal metallic particles[7] finely dispersed in water. The colloidal suspension must be stabilized by highly water soluble protective agents such as polymers,[8] surfactants[9] or ionic species[10] to prevent aggregation and to facilitate recycling. Recently, our laboratory described hydrogenation of alkenes by colloidal suspension of rhodium(0) stabilized by trisulfonated molecules.[11]

Here we describe the complete hydrogenation of various benzene derivatives under biphasic liquid–liquid (water/hydrocarbon) systems by protected rhodium(0) colloids. This metal is known to reduce arenes[12] but to our knowledge, this is the first example allowing an efficient conversion with recycling at room temperature and under atmospheric hydrogen pressure.

In this system, the catalytically active aqueous suspension is made of metallic rhodium(0) particles prepared by reducing rhodium trichloride with sodium borohydride in dilute aqueous solutions of hydroxyalkylammonium salts **1a–d** (Scheme 1). These compounds, easily synthesized[13] by quaternization of *N,N*-dimethylethanolamine with the appropriate bromoalkanes, are highly water soluble. Surface tension measurements† of compounds **1a–1d** show that they are surfactants and self aggregate into micelles at critical micellar concentrations (cmc) of 1×10^{-2}, 2.5×10^{-3}, 1×10^{-3} and 2.5×10^{-4} mol l^{-1}. The interfacial tensions of aqueous solutions decreased from 72 to *ca.* 37 mN m^{-1}. Nevertheless, only **1c** and **1d** (alkyl chain containing 16 and 18 carbons) are efficient protective colloid agents for rhodium nanoparticles with an effective electrosteric stabilization. Transmission electron cryomicroscopic observations‡ show that the average particle size of system Rh–**1c** was 3.6 nm. The size distribution histogram was obtained on the basis of measurement of about 300 particles (Fig. 1). No evolution of distribution was observed after catalysis, consequently, these monodispersed aqueous suspensions are highly stable and can be re-used for further runs.



1a *n* = 1
1b *n* = 3
1c *n* = 5
1d *n* = 7

Scheme 1

The hydrogenation of benzene derivatives using the catalytic system (Rh/**1c–d**/water) under biphasic conditions is very selective and gives the corresponding cyclohexanes. Stable suspensions prepared in the presence of surfactant **1c** or **1d** with an optimized molar ratio **1c**,**d**/Rh = 2 give a better activity and prevent aggregation. This sytem is sufficient to maintain colloidal particles within the aqueous phase during the catalytic process and thus allows its recycling. In contrast with **1c**, CTAB (cetyltrimethylammonium bromide) gives poor results during recycling (Table 1, entry 9). This justifies the use of the hydroxyalkylammonium salt **1**. No hydrogenated intermediates are observed during the catalysis. The reaction is monitored by the volume of hydrogen consumed and gas chromatographic analysis. The conversion is usually complete after 7 h (Table 1). No induction period is observed but steric and electronic effects of substituents affect the reaction time and arenes substituted by electron-withdrawing groups react slowly (Table 1, entry 12) or not (Table 1, entry 13) whereas the reaction is favoured with electron-donating substituents. In the latter case the substrate should be preferentially adsorbed on the colloid (Table 1, entries 1–11). Analogous effects have been observed by Lemaire and coworkers.[5] The chemoselectivity of the reaction is good, with ester and ether functions remaining unaffected (Table 1, entries 6 and 12). In addition to the hydrogenation of

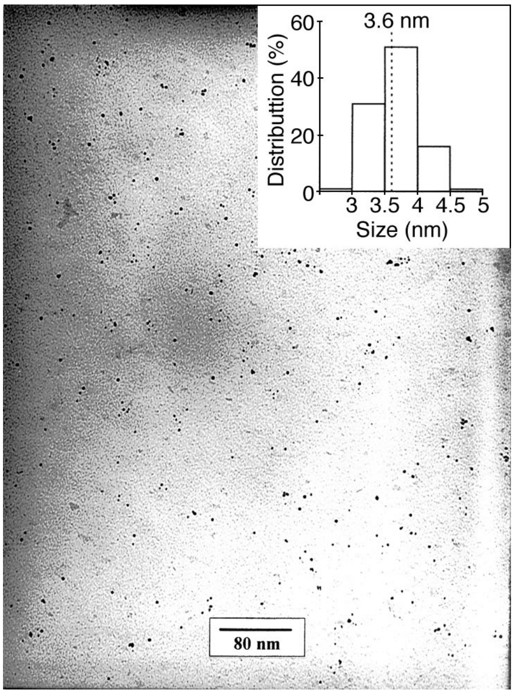


Fig. 1 TEM of Rh nanoparticles stabilized by **1c**.

Table 1 Hydrogenation of benzene derivatives under biphasic conditions[a]

					1st Run		2nd Run	
Entry	Substrate	Stabilizing agent	Substrate/Rh^0	Product yield (%)[b]	*t*/h	TOF[c]/h^{-1}	*t*/h	TOF[c]/h^{-1}
1	Benzene	**1c**	100	Cyclohexane (100)	5.3	57	6.2	48
2	Benzene	**1d**	100	Cyclohexane (100)	9.1	33	13.3	23
3	Toluene	**1c**	100	Methylcyclohexane (100)	5.7	53	6.9	43
4	Ethylbenzene	**1c**	100	Ethylcyclohexane (100)	6.9	43	7.4	40
5	Cumene	**1c**	100	Isopropylcyclohexane (100)	7.8	38	8.6	35
6	Anisole	**1c**	100	Methoxycyclohexane (100)	5	60	5.3	57
7	Anisole	**1c**	500	Methoxycyclohexane (100)	23	65	24	63
8	Anisole	**1d**	100	Methoxycyclohexane (100)	8.4	36	11.5	26
9	Anisole	**CTAB**	100	Methoxycyclohexane (100)	5.1	59	24	13
10	Phenol	**1c**	100	Cyclohexanol (100)	5.2	58	5.7	53
11	Phenol	**1d**	100	Cyclohexanol (100)	5.6	54	8.4	36
12	Ethyl benzoate	**1c**	100	Ethyl cyclohexanoate (100)	9.5	32	11.9	25
13	Bromobenzene[d]	**1c**	100	—	—	—	—	—
14	Aniline	**1c**	100	Cyclohexylamine (100)	10	30	—	—
15	Styrene	**1c**	100	Ethylcyclohexane (100)	7.3	55	8.4	48
16	*o*-Xylene	**1c**	100	1,2-Dimethylcyclohexane *cis* (95), *trans* (5)	7.5	40	8.9	34
17	*m*-Xylene	**1c**	100	1,3-Dimethylcyclohexane *cis* (87), *trans* (13)	7.3	41	8.5	35
18	*p*-Xylene	**1c**	100	1,4-Dimethylcytclohexane *cis* (70), *trans* (30)	7.1	42	8.2	37

[a] *Conditions*: catalyst (3.8×10^{-5} mol), surfactant (7.6×10^{-5} mol), water (10 ml), substrate (3.8×10^{-3} mol), hydrogen pressure (1 atm), temperature (20 °C), stirred at 1500 min^{-1}. [b] Determined by GC analysis. [c] Turnover frequency defined as mol of H_2 per mol of rhodium per h. [d] Similarly PhI, PhCl and PhF are not reduced.

the aromatic ring, *exo*-C–C double bonds are hydrogenated (Table 1, entry 15). A complete hydrogenation is also observed with disubstituted benzene derivatives (Table 1, entries 16–18). The *cis*-compounds are largely the major products as usually observed in heterogeneous catalytic systems.[14] Finally, we have observed the formation of cyclohexylamine by reduction of aniline (Table 1, entry 14) but in this case, the colloidal suspension is insufficiently stable and aggregates. Accordingly the catalytic activity during the second run dramatically decreases to become negligible. We suggest a reaction between the product and the surfactant.

The durability of the catalytic system was tested by using it for four successive hydrogenations of anisole. In the first cycle, the turnover frequency (TOF) was 60 h^{-1}. Then, the aqueous phase containing the catalyst was separated from the hydrogenated product by simple decantation and re-used in a second hydrogenation cycle. In the same manner the catalyst was recycled for a third and fourth run. The aqueous suspension shows a comparable turnover activity during the four runs of catalysis. As the activity during recycling depends on the amount of colloidal particles which remain in water after decantation, an efficient biphasic catalytic system with good remaining activity at the fourth run is a demonstration of the stability of the catalytically active suspensions with compound **1c**.

In conclusion, these results show that rhodium nanoparticles, protected by hydroxyalkylammonium salts containing at least 16 carbons leading to electrosteric stabilization, can be readily used for quantitative reduction of arenes. The interfacial tension parameter can be modulated to favour the contact between the catalyst and the substrate localised in two phases. Finally, we describe an efficient recycling process for hydrogenation of benzene derivatives without loss of activity and usable under standard conditions (20 °C, 1 atm H_2).

We thank CNRS and the Region Bretagne for financial support. We would also like to thank Dr Rolland (University of Rennes 1) for helpful comments and TEM micrographs.

Notes and references

† Surface tension measurements were performed at 20 °C using the ring method with a Du Nouy tensiometer (Krüss K10T).

‡ TE Cryo-Microscopic studies were conducted using a PHILIPS CM 12 transmission electron microscope at 100 keV. Samples were prepared by a dropwise addition of the stabilized colloid in water onto a copper sample mesh covered with carbon. The colloidal dispersion was removed after 1 min using cellulose, then the samples were quickly frozen in liquid ethane before transfer to the frozen microscope.

1 A. Stanislaus and B. H. Cooper, *Catal. Rev.*, 1994, **36**, 75.
2 K. Weissermel and H. J. Arpe, in *Industrial Organic Chemistry*, VCH, New York, 2nd edn, 1993, p. 343.
3 S. Siegel, in *Comprehensive Organic Synthesis*, ed. B. M. Trost and I. Fleming, Pergamon Press, New York, 1991, vol. 9; H. Pines, *The Chemistry of Catalytic Hydrocarbon Conversions*, Academic Press, New York, 1981; M. S. Eisen and T. J. Marks, *J. Am. Chem. Soc.*, 1992, **114**, 10 358; R. D. Profilet, A. P. Rothwell and I. P. Rothwell, *J. Chem. Soc., Chem. Commun.*, 1993, 42; M. A. Keane, *J. Catal.*, 1997, **166**, 347; H. Gao and R. J. Angelici, *J. Am. Chem. Soc.*, 1997, **119**, 6937.
4 J. S. Yu, B. C. Ankianiec, M. T. Nguyen and I. P. Rothwell, *J. Am. Chem. Soc.*, 1992, **114**, 1927; I. P. Rothwell, *Chem. Commun.*, 1997, 1331; L. Plasseraud and G. Süss-Fink, *J. Organomet. Chem.*, 1997, **539**, 163.
5 K. Nasar, F. Fache, M. Lemaire, J. C. Béziat, M. Besson and P. Gallezot, *J. Mol. Catal.*, 1994, **87**, 107; F. Fache, S. Lehuede and M. Lemaire, *Tetrahedron Lett.*, 1995, **36**, 885; K. S. Weddle, J. D. Aiken III and R. G. Finke, *J. Am. Chem. Soc.*, 1998, **120**, 5653 and references therein.
6 For example, see: B. Cornils and W. A. Herrmann, in *Aqueous-Phase Organometallic Catalysis*, Wiley–VCH, Weinhem, 1998; W. A. Herrmann and C. W. Kohlpaintner, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1524; B. Cornils, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1575.
7 G. Schmid, in *Clusters and Colloids*, VCH, Weinheim, 1994, p. 459; L. N. Lewis, *Chem. Rev.*, 1993, **93**, 2693.
8 C. W. Chen and M. Akashi, *Langmuir*, 1997, **13**, 6465; A. B. R. Mayer and J. E. Mark, *J. Polym. Sci., Part A: Polym. Chem.*, 1997, **35**, 3151; L. M. Bronstein, S. N. Sidorov, A. Y. Gourkova, P. M. Valetsky, J. Hartmann, M. Breulmann, H. Cölfen and M. Antonietti, *Inorg. Chim. Acta*, 1998, **280**, 348.
9 T. Yonezawa, T. Tominaga and N. Toshima, *Langmuir*, 1995, **11**, 4601; Y. Berkovich and N. Garti, *Colloids Surf., Part A: Physicochem. Eng. Asp.*, 1997, **128**, 91.
10 C. Larpent and H. Patin, *J. Mol. Catal.*, 1988, **44**, 191.
11 C. Larpent, E. Bernard, F. Brisse-Le Menn and H. Patin, *J. Mol. Catal.*, 1997, **116**, 277.
12 O. N. Efimov, O. N. Ermenko, A. G. Ovcharenko, M. L. Khidekel and P. S. Chekrii, *Bull. Acad. Sci., USSR, Chem. Sect.*, 1969, 778; K. R. Januszkiewicz and H. Alper, *Organometallics*, 1983, **2**, 1055; J. Blum, I. Amer, K. P. C. Vollhardt, H. Schwarz and G. Höhne, *J. Org. Chem.*, 1987, **52**, 2804.
13 G. Cerichelli, L. Luchetti, G. Mancini and G. Savelli, *Tetrahedron*, 1995, **51**, 10 281.
14 H. Nagahara, M. Ono, M. Konishi and Y. Fukuoka, *Appl. Surf. Sci.*, 1997, **121**/**122**, 448.

Communication 9/00551J