REDUCTION BY DISSOLVING BIMETALS

T. Mallát,[*] Zs. Bodnár and J. Petró

Department of Organic Chemical Technology, Technical University of Budapest, H-1521, Budapest, Hungary

Abstract. The rate and selectivity of reductions of various organic functional groups by dissolving metals can be influenced by cementation of a second metal onto the surface of the base metal. Pb, Pd or Ni deposition onto Zn, Al or Fe had a significant effect.

INTRODUCTION

The classic method of reduction, using dissolving metals (e.g. Zn, Al or Fe) in an acidic or alkaline medium has been partly replaced by newer and more efficient procedures. There are, however, indications that by applying dissolving bimetallic systems the old method may be improved for several purposes[1-5].

It has been observed over a long period of time that the rate and selectivity of the reduction may be increased by pretreating the metal[6-7]. These treatments may be devided into two categories. In the first the aim is to remove the oxide layer from the metal surface with an acid (HCl) or metal halide (e.g. $AlCl_3$, NH_4Cl, $ZnCl_2$). Metal corrosion is greatly enhanced in the presence of Cl-ion, although this may involve complex effects[8]. In the second method, the properties of the dissolving metal are modified by a second metal. Classic examples of this category are: Zn + Cu, Zn + Hg, Al + Ni (Raney alloy), Al + Hg, however other metals, such as Ag, Cd or Pt were also used as modifiers[7,9-11]. The simplest way of preparing such a bimetallic system is by reductive deposition of the second metal (cementation) from its dissolved salt onto the surface of the "base" metal (Zn, Al or Fe)[1-3]. The aim of our investigations was to prove that this technique is generally suitable for influencing rates and selectivities of dissolving metal reductions.

RESULTS AND DISCUSSION

The preparation of bimetallic system by cementation may be planned with prior knowledge of the Nersnt potentials of metal/metal ion systems. Metal ions having positive electrode potentials with respect to the base metal, may be discharged and deposited onto the surface as (bulk) metals. If the two metals interact, monolayer or submonolayer

deposition ("adsorbed metal") is possible above the Nernst potential of the second metal. The characteristics of adsorbed metals formed by underpotential deposition are reviewed elsewhere[12].

Thus, after cementation the base metal will be partly covered by the second metal, as can be checked e.g. by an electron microscopic measurement (Fig.1). During treatment with $HgCl_2$ (amalgamation), bulk alloy formation is also possible, due to the high mobility of Hg. It was found earlier[10], that a Zn_2Hg phase was formed on the surface of amalgamated Zn, and this structure was assumed to be responsible for the four electron transfer reduction of acetophenone to ethylbenzene.

Figure 1. a:Pd (light) deposition on Al (dark) powder (Enlargement:550X)
b:Pd (light) deposition on Zn (dark) powder (Enlargement:5500X)

A change in the surface structure and composition of dissolving metal should influence the reduction of organic molecules. An example is provided by the selective hydrodehalogenation of 7,7-dichloro-bicyclo(3,2,0)hept-2-en-6-one (1) to bicyclo(3,2,0)hept-2-en-6-one (2) (1 and 2 are intermediates in PGF_2 synthesis (Scheme 1).
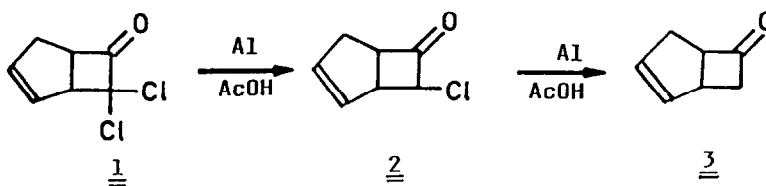
Scheme 1.

The results in the Table 1 refer to an intermediate reaction stage, when the conversion of 1 is total, but intermediate product 2 is still present. Addition of lead-, cadmium- or tin-salts to the reaction mixture increases the rate of reaction (and also the finel yield[3]). Nickel-, iron- or copper-salts slightly lead to an increase in rate, but

selectivity (C=C bond saturated) decreases.

Table 1. Hydrodehalogenation of $\underline{1}$ to $\underline{3}$ by (Al + M) systems.

product composition, %		
M	$\underline{2}$	$\underline{3}$
–	58	41
Pb	2	95
Cd	16	81
Sn	29	70
Fe	38	51
Cu	41	48
Ni	49	4
Hg	63	35

Table 2. Dehalogenation of 2-iodoaniline $(\underline{4})$ and 4-chlorophenol $(\underline{5})$ by Zn + M system.

	yields, %	
M	aniline	phenol
–	44	0
Pb	36	0
Cd	36	0
Sn	35	–
Cu	30	0
Ni	25	0
Tl	25	–
Co	17	0
Hg	3	0
Fe	1	0
Pd	–	69

Explanation of the result is not simple, because several reaction parameters are influenced by the formation of the bimetallic system. An important factor is the hydrogen overvoltage of the dissolving metal[13]. Hg, Pb or Sn deposition on the base metal increases hydrogen overvoltage, thus suppressing hydrogenation side reactions. Not only the saturation of the C=C bond, but also the hydrogen evolution is suppressed by the Al + Pb system, related to that of Al alone.

The opposite is true for Cu, Fe and especially for Ni deposition. The Nickel deposited on the Al surface behaves as a Ni catalyst, and dissolution of Al produces the electrons for the discharge of protons leading to dehalogenation of $\underline{1}$ and $\underline{2}$.

Surface deposition of the second metal may change the adsorption of the organic molecule, the free surface area and the rate of dissolution of the base metal, etc. Such an effect may cause the difference between Hg and Pb deposition, since hydrogen overvoltage for the two metals is similar. The exact interpretation of the reaction rate is not easy, since various reaction steps may be rate determining, and the mechanism may change with different reducing bimetals.

Treatment of the dissolving metal with $HgCl_2$ or $CuCl_2$ may not be generally considered to be an activation process. Moreover, cementation of any second metal onto the surface of the base metal may lead to a decrease in the rate of reaction. Kinetic data (yields after 45 min) of the hydrodehalogenation of 2-iodoaniline are collected in Table 2. Ni or Pd usually catalyse hydrodehalogenation, whereas I^- ion poisons the catalysts. Zn + Pd or Al + Pd bimetals are excellent reducing systems for Cl-removal: see e.g. dehalogenation of

4-chlorophenol, in Table 2. As is well known[14], Pd has the highest hydrodehalogenation activity of hydrogenation catalysts.

The X + Ni system, where X: Al, Zn or Fe, exhibits outstanding activity and selectivity in some reactions[1]. Examples of the reduction of simple organic molecules having various functional groups are shown in Table 3. Yields are ca. 1-1.5 orders of magnitude higher when a dissolving.bimetal system was used, instead of the base metal. Consequently, reduction of the organic molecule takes place mainly on the surface of the Ni deposit. Dissolution of the base metal supplies the electrons for the reduction of the organic molecule. If the rate of reduction of the organic functional group is negligible on the surface of the base metal (e.g. hydrogenolysis of benzyl alcohol), the overall process may be considered as a transfer hydrogenation. Otherwise, concurrent reactions take place on both metals.

Beneficial use of the Al + Ni system (Raney alloy) was discovered several decades ago. The significance of our method lies on the fact that other bimetallic systems, e.g. Fe + Ni or Zn + Pd, are not available commercically.

All the bimetallic systems discussed above were prepared simply by adding the metal salt to the reaction mixture. The only exception was Ni. When Ni was deposited from an aqueous Ni salt solution by, e.g. Al, the bright powder turned black in 0.5-1 min, and was folloved by intensive hydrogen evolution, the colour of Ni salt being preserved. Ni deposited onto the surface of Al, eliminates the high hydrogen overvoltage. The Ni/Ni^{2+} system has a Nernst potential negative to that of the H/H^+ system, thus hydrogen evolution replaced the discharge of Ni^{2+} ions. Total Ni deposition can be achieved by replacing water with a polar organic solvent, e.g. ethanol, in which Nernst potentials are different.

Table 3. Reduction of various functional groups by X + Ni systems

Reagent	Product(s)	X	$T, {}^{o}C$ by (X+Ni)	Yields, %	by X
$PhCH_2-OH$	$PhCH_3$	Al	25	100	0
$PhCH_2-Cl$	$PhCH_3$	Al	25	98	5
$PhCOCH_3$	$PhCH_2(OH)CH_3$	Al	20	90	10
	$PhCH_3$			10	0.2
$PhC\equiv CH$	$PhCH=CH_2$	Al	40	59	17
	$PhCH_3$			18	2
2-tolunitrile	2-tolualdehyde	Fe	80	95	2
c.hexanone	c.hexanole	Al	20	55	5

The rate of reduction is a function of base metal to second metal ratio, and a total

pre-deposition of Ni increases the reaction rate by a factor of 3-10, depending on the type of functional group to be reduced.

Finally, the term "dissolving bimetal reduction" requires some explanation. Dissolution of the second metal is negligible, if the difference between electrode potentials of the two metals is higher than 0.1-0.2 V (this case occurs most frequently). Only the base metal is dissolved during the reaction. When all the base metal in a single small particle has been completely consumed, the second metal of the more positive Nerst potential is also dissolved and can be deposited again on another base metal particle.

EXPERIMENTAL

The metal salts used were: $Pb(OAc)_2.3H_2O$, $Cd(OAc)_2.2H_2O$, $SnCl_2$, $FeCl_3.6H_2O$, $CuCl_2.2H_2O$, $NiCl_2.6H_2O$, $HgCl_2$, K_2PdCl_4, $TlNO_3$, $Co(OAc)_2.4H_2O$. After dissolving bimetal reductions, mixtures were filtered. Product composition was determined by GLC, after extraction (CH_2Cl_2 or CCl_4) and drying (Na_2SO_4). 2-Tolualdehyde was determined as 2,4-dinitro-phenylhydrazone.

The scanning electron microscopic measurements were carried out with an ISI Super IIIA type microscope fitted to a energy-dispersive X-ray spectrometer.

Hidrodehalogenation of 7,7-dichloro-biciclo(3,2,0)hept-2-en-6-one (1). 10.5 g (59 mmol) freshly distilled 1 (98-99 % of 1), 40 cm^3 water, 1 g metal salt and 6 g (223 mmol) Al powder were mixed at 70 ^{O}C (n= 800 min^{-1}), and 20 cm^3 (350 mmol) AcOH diluted with 28 cm^3 water was added droppwise during 3 h.

Hydrodehalogenation of 2-iodoaniline (4). 2.2 g (10 mmol) 4, 20 cm^3 MeOH and 3 cm^3 (53 mmol) AcOH were mixed at 20 ^{O}C and 1.3 g (20 mmol) Zn powder was added during 30 min. After 15 min the slurry was filtered.

Hydrodehalogenation of 4-chlorophenole (5). 1.78 g (15 mmol) 5, 0.5 mmol metal salt, 20 cm^3 (350 mmol) AcOH, 1.2 cm^3 water and 5 g (78 mmol) Zn powder were mixed at 11o ^{O}C (reflux) for 2 h.

Reduction of benzyl alkohol (6). 2 g (74 mmol) Al powder, 2 g (8.4 mmol) $NiCl_2.6H_2O$ and 20 cm^3 EtOH were mixed at 60-65 ^{O}C until the green colour disappeared (8-10 min). The slurry was cooled to 25 ^{O}C , followed by the addition of 5 cm^3 (49 mmol) 6 and 20 cm^3 water. Then 18 cm^3 (200 mmol) 36 wt% HCl was added droppwise and stirred for 1 h. After 0.5 h the slurry was filtered.

Reduction of benzyl cloride (7). Al + Ni bimetal was prepared as above. 5 cm^3 (43 mmol) 7 and 20 cm^3 water were added at 25 ^{O}C and 5 cm^3 (92 mmol) H_2SO_4, diluted with 31 cm^3 water was added droppwise in 3 h.

Reduction of acetophenone (8). The procedure was similar to the reduction of 7, with the exception that 5 cm^3 (29 mmol) 8 was used, as a reactant and 18 cm^3 (200 mmol) 36 wt% HCl was added droppwise at 20 ^{O}C .

Reduction of phenylacetylene (9). 3 g (111 mmol) Al powder, 2 g (8.4 mmol) $NiCl_2.6H_2O$

and 20 cm^3 EtOH were mixed at 60-65 ^{O}C until the green colour disappeared. 5 cm^3 (46 mmol) **9**, 10 cm^3 water and 20 cm^3 EtOH were added and 27 cm^3 (300 mmol) 36 wt% HCl was dripped into the slurry in 3 h. Reaction time was 3.5 h.

Reductive hydrolysis of 2-tolunitrile (10). 6 g (108 mmol) Fe powder, 2 g (8.4 mmol) $NiCl_2.6H_2O$ and 10 cm^3 water were mixed at 85 ^{O}C for 10 min. 20 cm^3 MeOH, 6cm^3 water, 12 cm^3 (0.21 mmol) AcOH and 5.3 g (45 mmol) **10** were added and mixed at reflux temperature for 40 min.

Reduction of cyclohexanone (11). The procedure was similar to the reduction of **8**, except for the use of 5 cm^3 (32 mmol) 11 as reactant.

<div align="center">REFERENCES</div>

1. Mallát, T.; Bodnár, Zs; Petró, J., Hung. Patent Appl. 1986, 3920.
2. Petró, J.; Mallát, T.; Soos, R.; Turcsán, I.; Nemes, J.; Szelestyei, M.; Vidra, L., Brit. Patent 1986, 2141426; Fr. Patent 1988, 8405891.
3. Mallát, T; Petró, J., Hung. Patent 1989, 1997665.
4. Petrier, C.; Luche, J.L., Tetrahedron Lett. 1987, 28, 2347 and 2351.
5. Hazarika, M.J.; Barua, N.C., Tetrahedron Lett. 1989, 30, 6567.
6. House, H.O., Modern Synthetic Reactions, Benjamin, New York, 1965.
7. Houben-Weil, Methoden der Organischen Chemie, 4/1c, Reduction I. G. Thieme, Stuttgart, 1980.
8. Nakabayashi; Tadaaki., J. Am. Chem. Soc. 1960, 82, 3900.
9. Theilheimer, W., Synthetic Methods of Organic Chemistry, S. Karger, Basel, 1958, 12, 919.
10. Horner, L.; Schmidt, E., Liebigs Ann. Chem. 1978, 1617.
11. Clark, R.D.; Heathcock, C.H., J.Org. Chem. 1976, 41, 636.
12. Kolb, D.M., Adv. in Electrochem. and Electrochem. Eng. 1978, 11, 125.
13. Brewster, J.H., J. Am. Chem. Soc. 1954, 76, 6361.
14. Freifelder, M., Practical Catalytic Hydrogenation, Wiley, New York, 1971.