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Homogeneous electromediated reduction of the 2-cyclohexen-1-one by transition metals

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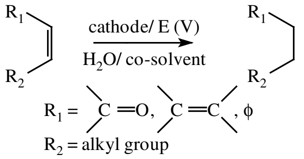
Abstract—The reduction of the 2-cyclohexen-1-one, mediated by some transition metal ions (Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+} and Fe^{2+}) and complexes ($[Ni^{II}(bipy)]Br_2$ and $[Fe^{II}(bipy)]Br_2$, where bipy = 2,2′-bipyridine), was carried out by using a homogeneous electromediated system: sacrificial anode, nickel cathode, (0.2 M) NaI as supporting electrolyte and undivided cell. A constant current of <100 mA was applied with a maximum cell potential of 2.0 V. Cyclohexanone was the principal product in major cases yielding 98%. Cyclohexanol was also detected in some cases. The selectivity of the process can be controlled by choosing Ni as mediator and Zn or Ni as sacrificial anode. A more reactive system can be reached when Fe sacrificial anode is used, giving cyclohexanol as major product (87%).

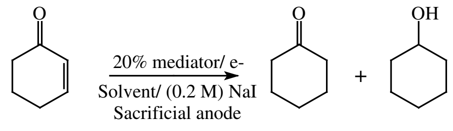
Several nickel complexes have been described to be able to mediate the reduction of various types of covalent bonds present in organic compounds.[1] The homogeneous catalysis of bidentate $Ni^0(L_1)$ complexes (where L_1 = 2,2′-bipyridine (bipy), 1,10-phenantroline or 1,2-bis(diphenylphosphino)-ethane) and tetradentate $Ni^I(L_2)$ complexes (where L_2 = cyclam or salem), has been largely studied from a mechanistic[2,3] and synthetic[1] point of view. Ni^0(bipy) complexes have been applied to reductive homo-coupling of halopyridinic compounds,[4,5] and reductive cleavage of N–O bonds, of isoxazolines.[6] Recently, the π-bond reduction of conjugated olefins was described, using Ni^0L_1 complex as catalyst in the presence of $NaBH_4$.[7] The electrocatalytic hydrogenation (ECH) of organic compounds has also been intensively studied in heterogeneous surface (Scheme 1).[8,9]

The principal advantage of the ECH process is the electrochemical generation of adsorbed hydrogen, directly on the cathode surface. Several deposited cathode materials (Pt, Pd, Rh, Ni, etc.) were described to be able to catalyze the hydrogenation reaction of many organic substrates.[10,11]



Scheme 1. Heterogeneous electrocatalytic hydrogenation of olefins.

In this work, we have studied the development of reaction conditions for homogeneous electromediated reduction (indirect hydrogenation) of unsaturated organic substrates in DMF. The 2-cyclohexen-1-one was used as olefinic standard, and some transition metal ions, and complexes, were tested as mediator for reduction of the π-bond (Scheme 2).



Scheme 2. Homogeneous electromediated reduction of the 2-cyclohexen-1-one.

Keywords: Electrochemical system; Mediated reduction; Olefins; Ketones.

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The electrochemical system was composed by an undivided cell (three entries), sacrificial anode, nickel cathode and inert gas (N_2), necessary to expel dissolved oxygen, which may be electrochemically reduced. NaI was used as supporting electrolyte. A pre-electrolysis is necessary to diminish the initial solution resistance,[5,6] by oxidative dissolution of metallic ions from sacrificial anode, while 1,2-dibromoethane is reduced on the cathode, giving ethene plus bromide:[12]

$$\text{anode: } M \rightarrow M^{2+} + 2e^-$$

$$\text{cathode: } CH_2Br\text{–}CH_2Br + 2e^- \rightarrow CH_2{=}CH_2 + 2Br^-$$

$$\text{in solution: } M^{2+} + 2Br^- \rightarrow MBr_2$$

After pre-electrolysis, 2-cyclohexen-1-one was added along with 0.2 equiv of mediator. The electrolyses were maintained with 100 mA (or less) constant current (cell potential should be lower than 2.0 V, to avoid the direct reduction of the substrate on the cathode surface), until its total consumption. The reaction products were determined by GC and GC–MS analysis, and yields by addition of internal standard.[12]

Table 1 shows some results obtained from homogeneous electromediated reduction (HEMR) of the 2-cyclohexen-1-one. Seven different catalysts were tested; five transition metal ions from family B (fourth period) of the periodic table: Zn^{2+}, Cu^{2+}, Co^{2+} Ni^{2+} and Fe^{2+}; and two complexes: $[Ni^{II}(bipy)]Br_2$ and $[Fe^{II}(bipy)](SO_4)$. The metal used as sacrificial anode was the first parameter investigated. The zinc showed to be inactive in DMF and no reduction product was observed (Table 1, entry 1). This result allowed us to use Zn, as sacrificial anode, and verify the mediator activity of other metallic ions. All other metals (Table 1, entries 2–5), including the complexes tested (Table 1, entries 6 and 7), presented reductive activity, giving cyclohexanone as main product. Some good results were observed with Ni^{2+}, Co^{2+} and Fe^{2+} ions. The electron transfer from cathode to the organic substrate, mediated by these metallic ions, that is, electrochemical efficiency (E.E.) of the process, is low. It should occur due to the slow deposition of the metallic ion on the cathode surface and proton deficiency in the reaction medium. $[Ni^{II}(bipy)]Br_2$ and $[Fe^{II}(bipy)]Br_2$ complexes were tested, trying to avoid the mediator deposition. The results showed the same selectivity and E.E., but yields were increased to 81% and 86%, respectively.

Entries 8 and 9 (Table 1) show experiments in the presence of sacrificial anode of Ni and Fe. It was observed a reactivity increase in the presence of iron ions, continuously added to the system from sacrificial anode, where high yield of the total hydrogenation product, cyclohexanol, was detected. The same behaviour was observed when Ni sacrificial anode was used, but in this case the selectivity was maintained, and a high yield of cyclohexanone was observed (Table 1, entries 8 and 10).

Some experiments were repeated in the presence of water (3 mmol), giving an electrochemical efficiency increase, when nickel is used as sacrificial anode, at the same time reasonable quantity of cyclohexanol was detected, showing a loss of selectivity. A tetrabutylammonium salt (TBABr) was also used as supporting electrolyte in DMF, giving similar results as one reported in Table 1, entries 6 and 9.

The interesting reducing behaviour of iron complex in DMF solution has already been reported by Durandetti et al.,[13,14] using $[Fe^{II}(bipy)_3]^{2+}$ as mediator in electrochemical reactions of α-chloroesters and allylic acetates with carbonyl compounds. The proposed mechanism involves a Fe^+ intermediary, which efficiency is increased

Table 1. Homogeneous electromediated reduction of (1.5 mmol) 2-cyclohexen-1-one in 20 mL DMF + (0.2 M) NaI, nickel cathode, using sacrificial anode and 100 mA constant current

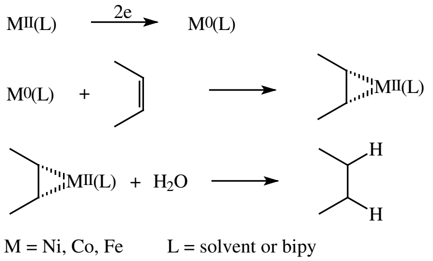
Entry	Mediator[a]/anode	Charge (C)	P1[b] (%)	P2[c] (%)	ee[d] (%)
1	Zn^{2+}/Zn	1200	—	—	—
2	Cu^{2+}/Zn	1500	11	—	02
3	Ni^{2+}/Zn	900	58	06	23
		2400	70	09	10
4	Co^{2+}/Zn	600	67	—	32
		1500	77	05	17
5	Fe^{2+}/Zn	600	64	06	36
		1800	69	06	13
6	$[Ni^{II}(bipy)]^{2+}$/Zn	1500	82	09	19
		2100	81	11	14
7	$[Fe^{II}(bipy)]^{2+}$/Zn	2100	86	07	14
		2400	78	15	12
8	Ni^{2+}/Ni	900	69	—	18
		1500	98	—	19
9	Fe^{2+}/Fe	900	08	80	54
		1500	06	87	35

[a] 20% of mediator was used.

[b] Cyclohexanone.

[c] Cyclohexanol.

[d] Electrochemical efficiency ($Q_{theoretical}/Q_{passed}$ × total yield).



Scheme 3. Proposed mechanism for olefin reduction mediated by metallic ions in aprotic solvent (DMF).

in the presence of 3 equiv of the ligand L_1. This mechanism is supported by the constant electrochemical potential which remained at the cathode (−1.1 V versus saturated calomelane electrode (SCE)), which corresponds to reduction of the Fe^{2+} complex into Fe^{+}.[15] As the 2-cyclohexen-1-one indirect reduction process, described in this work, occurs at more negative potentials (−1.5 V/SCE), we can propose that M^0 (M = Co, Ni and Fe) and M^0bipy (M = Ni, Fe) solvated species probably mediate the reduction of the olefin, as depicted in Scheme 3.

Solvated metallic ions and metal complexes should be reduced at the cell potential applied (~2.0 V), and in the presence of the 2-cyclohexen-1-one, π-bond is reduced giving an intermediary complex. The protonation of the metal–olefin complex should occur due to residual water presence or extraction step of the products, however the extraction performed with deuterated water gave no deuterated product.

In conclusion, the results obtained from homogeneous electromediated reduction of the 2-cyclohexen-1-one, by transition metals, show that it is possible to control the selectivity of the reduction process by varying parameters like sacrificial anode, mediator and water concentration.

Acknowledgements

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