# Electrocatalytic hydrogenation of substituted naphthalenes at Raney nickel electrodes in aqueous media

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## Introduction

Electrocatalytic hydrogenation (ECH) at Raney metal electrodes is a mild method for hydrogenating a variety of functional groups in slightly acidic (pH $\geq$ 3), neutral or basic aqueous or hydro-organic media.[1] It involves the reaction of chemisorbed hydrogen, M(H), with an adsorbed organic substrate as in catalytic hydrogenation (CH): $M(R) + 2M(H) \rightarrow RH_2 + M$, where R is an unsaturated compound and M represents an adsorption site on the electrode surface; or $M(RZ) + 2M(H) \rightarrow RH + ZH + M$, where RZ represents an organic substrate with a weak sigma bond (hydrogenolysis). In ECH, M(H) is generated by reduction of water: $2H_2O/H_3O^+ + 2e^- + M \rightarrow 2M(H) + 2HO^-/H_2O$. Thus the kinetic barrier for the thermal dissociation of dihydrogen, which must take place in CH, is bypassed and hydrogenations on R-metals can be carried out at temperatures below 100ºC and at atmospheric pressure.

We report on a study of the ECH of substituted naphthalenes **1** and **4** at Raney nickel electrodes in aqueous media (Schemes 1 and 2, X = $CH_3$, OH, $NH_2$). The aim was to determine the selectivity of the hydrogenation to substituted tetralins (hydrogenation of ring B *vs.* hydrogenation of ring A: **3**/**2** or **6**/**5** ratio = B/A ratio) as a function of substituent X and to see if ECH could be an efficient method for desulfurization of 2-thionaphtol (**7**) (Scheme 3).

## Results and Discussion

The electrolyses were carried out in a two-compartment jacketed H-cell with a cation-exchange Nafion membrane, on 2 mmoles of substrate (16 mM solution), at 80ºC, under gavalnostatic conditions (J = 0.8 or 1.7 mA/cm$^2$), and at Raney nickel electrodes consisting of Raney nickel particles imbedded in a Ni matrix.[2] Three media were used: 1) ***Neutral*** [ethylene glycol-water (1.5% $H_2O$ v/v) containing $H_3BO_3$ 0.1 M and NaCl 0.1 M, $pH_i$ = 3 and $pH_f$ = 6, $E_{Wi} = -0.64$ V and $E_{Wf} = -1.06$ V *vs.* SCE]; 2) ***Basic*** [ethylene glycol-water (1.5% $H_2O$ v/v) containing NaOH 0.14 M and NaCl 0.1 M, pH > 13, $E_{Wi} = -0.98$ V and $E_{Wf} = -1.09$ V]; 3) ***Micellar*** [catholyte: water containing 5% CTAB and NaCl 0.2 M, $pH_i$ = 6 and $pH_f$ = 10, $E_{Wi} = -0.77$ V and $E_{Wf} = -0.93$ V; anolyte: $H_2SO_4$ 0.1 M]. For the ECH of 2-thionaphtol (**7**), a pulse current was also used: J = 0.8 mA/cm$^2$ for 10 ms and J = 0 for 10 ms].

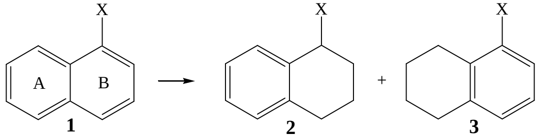
In ***basic*** medium, the ECH is inefficient for all substrates as shown by low current efficiencies and low conversion rates. In the case of naphtols **1** and **4** (X = OH), which are fully deprotonated at pH > 13, ring B is hydrogenated preferentially: B/A ratio of 4 for 1-naphtol and of 3 for 2-naphtol (conversion rates of 20-25%). In the case of aminonaphthalenes **1** and **4** (X = $NH_2$), ring A is hydrogenated faster: B/A ratio of 0 (100% regioselectivity) for 1-aminonaphthalene and of 0.3 for 2 aminonaphthalene (conversion rates of 30-50%). With the other substrates, only hydrogen evolution was observed.

In ***neutral*** medium, the ECH is more efficient than in basic medium: the current efficiencies (40-80%) for and conversion rates (70-90%) are higher (charge of 5 F/mol). The regioselectivity is the same as in basic medium but is generally lower: B/A ratio of 2.5 for 1-naphtol (**1**, X = OH), about 1 for 2-naphtol (**2**, X = OH), 0.4 for 1-aminonaphthalene (**1**, X = $NH_2$), and 0.3 for 2-aminonaphthalene (**2**, X = $NH_2$). In the case of methylnaphthalenes **1** and **4** (X = $CH_3$), the ECH is not regioselective (B/A ratio close to 1). The ECH of 2-thionaphtol (**7**) gives naphthalene (**8**) as the main product with some tetralin (**9**) with very low current efficiencies: 12% after 5 F/mol (22% conversion) and 5% after 42 F/mol (100% conversion). Interestingly, the amount of tetralin formed remains constant after a charge of 5 F/mol, which would indicate that the catalyst is deactivated towards the hydrogenation of naphthalene but retains some activity for the hydrogenolysis of the $Csp_2$−SH bond. By using a pulsed current, the efficiency is increased and more tetralin is formed: 36% current efficiency (50% conversion) after 5 F/mol and 12% current efficiency (100% conversion) after 21 F/mol.

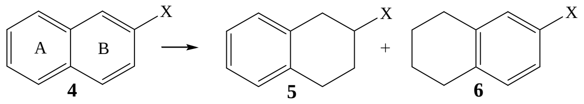
In **micellar** medium (neutral), the results are similar to those obtained in neutral ethylene glycol-water in terms of selectivity (B/A ratio), conversion rate, and current efficiency for the substituted naphthalenes **1** and **4** (X = $CH_3$, OH and $NH_2$). The ECH of 2-thionaphtol (**7**) is slightly more efficient and gives more tetralin. No electrolysis with a pulse current was carried out in the micellar medium.

In the ECH of 1-naphtol (**1**, X = OH), 1-tetralone, tetralin (**9**), and 2-(1-tetraloxy)ethanol are formed in small amounts besides compounds **5** and **6** shown in Scheme 1 and, in the ECH of 2-naphtol (**2**, X = OH), tetralin (**9**) is formed also. The mechanism of formation of these secondary products will be discussed.

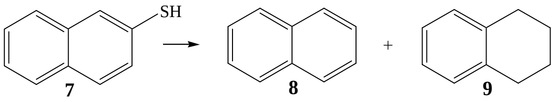
The results will be compared to those of catalytic hydrogenation on Raney nickel catalysts.



Scheme 1



Scheme 2



Scheme 3

## Acknowledgements

An acknowledgment is made to NSERC of Canada, FQRNT (FCAR) of Quebec., and the Université de Sherbrooke.

## References

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**2.** D. Robin, M. comtois, A. Kam Cheong, R. Lemieux, G. Belot and J. Lessard, *Can. J. Chem.*, **68**, 1218-1227 (1990).