

CATALYTIC REDUCTION OF UNSATURATED HALIDES BY
Ni(II) COMPLEXESA.L.R. Ataíde[§], A.P. Esteves[§], A.M. Freitas[§], M.J. Medeiros^{§*}, V. Mota[§],
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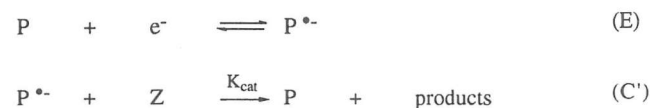
Abstract: Radical cyclisation is rapidly becoming an important method for the formation of cyclic systems. Hence, some electrochemical results obtained in the study of electroreductive intramolecular cyclisation of different types of unsaturated halides using nickel(II) complexes as mediators, are presented.

Keywords: radical cyclisation, nickel complexes.

Introduction

Radical cyclisation is emerging as one of the leading methods for the construction of cyclic systems [1-3]. While organotin reagents have dominated synthetic procedures involving radical chemistry over the last decade [3], problems associated with product purification, price and toxicity have stimulated interest in development of more user and environmentally friendly reagents.

A convenient alternative to the tin hydride method makes use of a Ni(II) complex as the electron transfer-catalyst [4]. This process is based on the following EC' mechanism:



in which the mediator (P) has a reduction potential positive to the substrate (Z) and is reduced at the electrode. The reduced mediator diffuses into the solution and reduces the substrate. The catalytic reaction recycles the mediator back to the electrode according to the kinetics of the system and to the relative concentrations of substrate and mediator (called the excess factor, $\gamma = [RBr]/[Ni^{II}L]$).

Results and Discussion

The Electrochemistry of Unsaturated Halides

Cyclic voltammograms were obtained at different scan rates at a vitreous carbon electrode for 4 mM solutions of 6-bromo-1-hexene **1** and (R)-(-)-citronellyl bromide **2** in DMF containing 0.1 M TBAB.

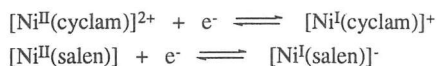
It was observed that both halides only showed one reduction wave at potentials near to -2.60 V (reductive cleavage of the carbon-bromine bond) which was highly irreversible.



The Reduction of the Ni (II) Complexes

Cyclic voltammograms were recorded at a series of potential scan rates between 0.020 and 0.200 V/s at a vitreous carbon electrode for solutions of [Ni(cyclam)](ClO₄)₂ and Ni(salen) complexes in DMF / TBAB (0.1 M). The voltammograms showed that both complexes underwent a reversible one-electron reduction to a stable product and that no further reduction occurred within the potential range of the medium. Formal electrode potentials are -1.36 V and -1.57 V vs Ag/AgCl for [Ni(cyclam)](ClO₄)₂ and Ni (salen), respectively.

Controlled potential electrolyses were also carried out at potentials just beyond the reduction peak for solutions of the complex. Linear plots of I against Q (charge) were obtained and extrapolation of these lines to I=0 gave *n* values close to one electron per molecule. Hence, all the data obtained indicate that the electrode reactions are:



where the added electron is nickel centred and the reduction is fast and occurs without significant changes in the geometry of the complex [5-7].

The Electrochemistry of the Ni (II) Complexes in the Presence of Unsaturated Halides

Figure 1 shows cyclic voltammograms recorded for solutions of [Ni(cyclam)](ClO₄)₂ in the presence of 6-bromo-1-hexene and citronellyl bromide.

In both cases the experiments show that addition of unsaturated halide to the Ni(II) complex solution results in the increase of the reduction peak height of the mediator and disappearance of the anodic wave. However, the increase in the cathodic peak current is not proportional to the concentration of unsaturated halide. The catalytic current is due, for both complexes, to the following mechanism (exemplified for [Ni^{II}L]²⁺):

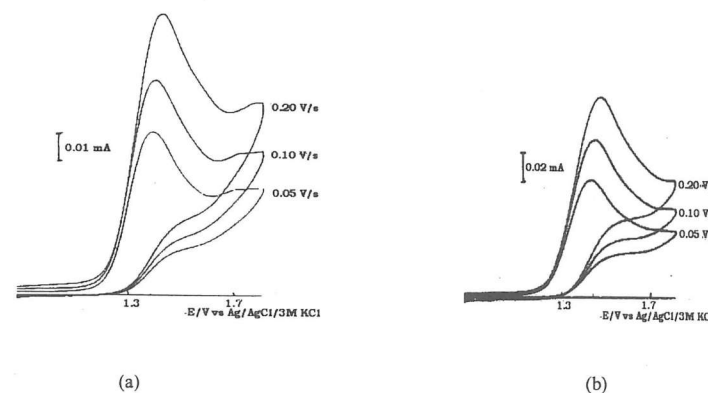
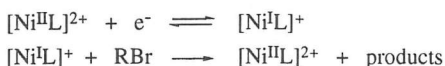


Figure 1 - Cyclic voltammograms for the reduction of 2.0 mM solution of [Ni(cyclam)](ClO₄)₂ in the presence of 6-bromo-1-hexene 8 mM (a) and citronellyl bromide 8 mM (b) in DMF containing 0.1 M TBAB at a vitreous carbon electrode (area. 0.070 cm²) and at scan rates indicated in the figure.

The data from these experiments for both Ni(II) complexes are presented in Table 1. From these data we can observe that the extent of the catalytic reaction increases when raising [RBr], for a given mediator concentration but it is higher in the case of Ni(cyclam)²⁺ than in the case of Ni(salen).

Table 1 - Data of the ratio I_c/I_d obtained from the cyclic voltammetry experiments of 2.0 mM Ni(II) complexes in DMF / 0.1 M TBAB in the presence of different concentrations of 6-bromo-1-hexene and citronellyl bromide. Potential scan rate 0.10 V/s.

Ni Complex	I _c /I _d					
	6-Bromo-1-hexene			Citronellyl Bromide		
	γ = 2	γ = 8	γ = 15	γ = 2	γ = 8	γ = 15
Ni(cyclam) ²⁺	2.79	4.84	6.46	3.89	7.01	8.18
Ni(salen)	1.55	2.02	2.15	1.68	2.03	2.25

I_c - catalytic peak current intensity of the catalyst in the presence of substrate
 I_d - peak current intensity of the catalyst in the absence of substrate
 γ = [RBr] / [Ni (II)]

Controlled-potential Electrolyses of Ni(II) Complexes in the Presence of 6-Bromo-1-hexene and Citronellyl Bromide

Table 2 shows results obtained from electrolyses of [Ni(cyclam)](ClO₄)₂ and Ni(salen) in DMF containing 0.1 M TBAB and 6-bromo-1-hexene or citronellyl bromide; the potential was set at

approximately 50 mV after the peak potential of the reduction wave of the catalyst in the presence of the unsaturated halide.

In the case of 6-bromo-1-hexene **1**, the desired carbocyclic product, methylcyclopentane **3**, was formed in quantities from 9-76%, depending on the concentration of unsaturated halide and of catalyst. The acyclic byproduct of this reaction, 1-hexene, appears in amounts from 3-10%.

In the case of citronellyl bromide **2**, the cyclised product, *p*-menthane (*cis* and *trans*) **4**, was formed in quantities from 43-55%. The acyclic byproduct of this reaction, 2,6-dimethyl-2-octene, also appeared in amounts of 16%.



Table 2 - Coulometric data and product distribution for reductions of 6-bromo-1-hexene and citronellyl bromide by Ni(I) complex electrogenerated at cathode in DMF containing 0.1 M TBAB.

RBr	Complex	WE	[RBr] mM	[Ni(II)] mM	n ^(a)	Product distribution ^(b)	
						Carbocyclic	Acyclic byproduct
1	Ni ^{III} L ²⁺ (c)	Vitreous carbon	2.5	2.5	1.3	76	—
			5.0	2.5	1.2	34	—
			2.5	1.25	1.2	65	—
			25.0	2.5	0.12 (d)	(d)	(d)
		Platinum	25.0	2.5	0.17 (d)	(d)	(d)
	Hg pool	15.0	3.0	—	9	10	
	Ni ^{III} L (e)	Vitreous carbon	5.8	2.9	1.2	31	—
		carbon	2.2	1.1	1.3	65	—
		Hg pool	6.7	1.3	1.3	22	3
2	Ni ^{III} L ²⁺ (c)	Platinum	3.4	1.3	1.4	53	16
			8.0	1.3	1.5	43	15

(a) Number of electrons per molecule of unsaturated halide; (b) Yields were determined by GC; (c) [Ni(cyclam)](ClO₄)₂: [1,4,8,11-tetraazacyclotetradecane]nickel(II) perchlorate; (d) Passivation of the cathode was observed; (e) Ni(salen): [2,2'-ethylenebis(nitrilomethylidene)diphenolate]nickel(II).

In conclusion : (i) The reaction of an unsaturated halide with the electrogenerated Ni(I) complex is always fast (the anodic peak of Ni(II) complex is absent), but the regeneration of the Ni(II) complex by the chemical sequence in the case of Ni(salen) is slower than in the case of the Ni(cyclam)²⁺ (the increase in peak current for the Ni(II) complex reduction is a measure of the rate at which the complex is regenerated); (ii) The reaction between the electrogenerated Ni(I) complex and the unsaturated halide is not a simple electron transfer but involves an inner sphere electron transfer.

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