Kinetic features of oxidative addition of organic halides to the organonickel σ-complex*

D. G. Yakhvarov, Yu. H. Budnikova,★ and O. G. Sinyashin

A. E. Arbuzov Institute of Organic and Physical Chemistry,
Kazan Research Center of the Russian Academy of Sciences,
8 ul. Akad. Arbuzova, 420088 Kazan, Russian Federation.
Fax: +7 (843 2) 75 2253. E-mail: yulia@iopc.knc.ru

Electrochemically generated organonickel σ-complexes were used as model compounds to study the kinetics of oxidative addition of ArNi^{I}bpy to RX, the key stage of cross-coupling of organic halides (RX). The reaction rate constants were calculated, and the sequence of relative reactivity of RX toward the electrochemically generated MesNi^{I}bpy complex was obtained.

Key words: nickel, 2,2´-bipyridine, organic halide, metal complex, electrochemistry, catalysis.

Studies of the mechanism of reductive transformations of organic halides in the presence of electrochemically generated low-valent transition metal complexes are of value for the theory and practice of catalysis.[1] We have previously[2,3] shown that the use of *ortho*-substituted aromatic bromides makes it possible to establish the structure of intermediates in RX dehalogenation by electrochemically generated Ni^{0}bpy complexes (bpy is 2,2´-bipyridine). Some intermediate organonickel compounds were isolated and characterized by physicochemical data, in particular, the product of the first stage of the catalytic cycle σ-MesNibpyBr complex. It is the product of the oxidative addition of MesBr to the electrochemically generated Ni^{0}bpy complex.[2,3] This complex is stable in air and is convenient for proving the occurrence of certain stages of the catalytic cycle.

It has been shown[2,3] that the key stage of catalytic RX dehalogenation resulting in cross-coupling products is the oxidative addition of RX to the electrochemically generated σ-MesNi^{I}bpy complex. The latter is formed by one-electron reduction of the σ-MesNibpyBr complex (Fig. 1).

$$\text{MesNi}^{II}\text{bpyBr} + \text{e} \underset{E_A}{\overset{E_C}{\rightleftharpoons}} \text{MesNi}^{I}\text{bpy} + \text{Br}^-$$

The purpose of this work is to estimate the reactivity of different RX toward the electrochemically generated MesNi^{I}bpy complex in cross-coupling reactions using cyclic voltammetry (CV).

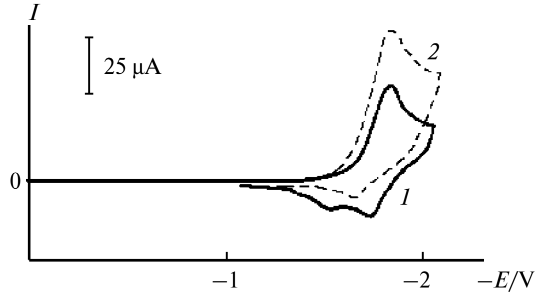

Fig. 1. CV curve for the MesNibpyBr complex (10^{-2} mol L^{-1}) in DMF against the background of Et_4NBF_4 (10^{-1} mol L^{-1}) in the absence (*1*, E_A) and presence (*2*, E_C) of RX.

The electrochemical behavior of MesNibpyBr was studied in the absence and presence of different RX. The CV curve for MesNibpyBr in DMF exhibits one one-electron reversible cathodic peak at −1.80 V. In addition to the anodic peak at −1.72 V related to this cathodic peak of the substrate ($i_A/i_C = 0.9$), a small anodic peak is observed at −1.50 V (see Fig. 1). Probably, the latter corresponds to the oxidation of the MesNi^{I}bpy—Ni^{I}Mesbpy dimer, which can form in the absence of RX.

Let us consider the shape of the CV curve for electroreduction of the MesNibpyBr complex at different amounts of RX. When RX is successively added to a solution of MesNibpyBr, the reduction current of the complex increases to a certain limit. At low RX concentrations the plot of the current *vs.* $\sqrt{C}_{RX}$ is linear, while in an excess of RX the current is independent of the concentration of the added substrate (Fig. 2). For the most part of substrates, the anodic component of the reduction peak of the MesNibpyBr complex disappears, *i.e.*, the electro-

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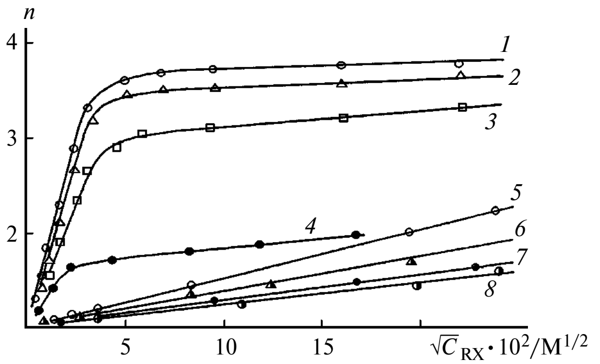
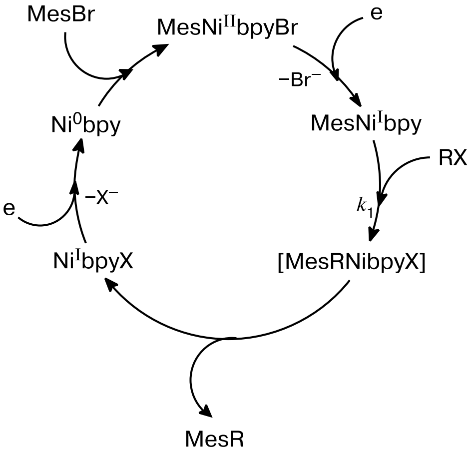


Fig. 2. Number of electrons (*n*) transferred at potentials of the reduction wave of MesNibpyBr as a function of $\sqrt{C}_{RX}$: *1*, Pr^iI; *2*, *i*-$C_5H_{11}I$; *3*, PhI; *4*, 2-ClTh; *5*, PhBr; *6*, 4-TolBr; *7*, BuBr; and *8*, MesBr.

chemically generated $MesNi^Ibpy$ complex enters into an irreversible chemical reaction, *viz.*, either oxidative addition or complexation with the substrate.



Subsequent reactions afford cross-coupling products if reductive elimination occurs rapidly. The current increase can be due to the catalytic reduction of intermediates of the cycle, which form upon elimination.

In the presence of MesBr, *o*-TolBr, and 2-ClTh (Th is thiophene), the cross-coupling reactions involving these compounds occur, most probably, slowly and the current increase of the cathodic peak (see Fig. 2) is caused by the reversible electrochemical reduction of the intermediate σ-[MesRNibpyX] complex, due to which the anodic component corresponding to this peak in the CV curve remains unchanged.

We made an estimate of the kinetics of the initial stage of the process (interaction of the σ-$MesNi^Ibpy$ complex with RX) under assumption that this stage is rate-determining. The k_1 rate constant was calculated from changes in the reduction current in the interval of RX concentrations in which the reduction current is proportional to $\sqrt{C}_{RX}$ and the reaction has the first order with respect to the substrate.[4] The calculated k_1 values are presented in Table 1. The slope of the plot $I = a\sqrt{C}_{RX} + b$ can characterize the rate of the primary stage of the process: the greater the slope, the higher the rate constant of the reaction of $MesNi^Ibpy$ with RX.

Table 1. Apparent rate constants for oxidative addition of organic halides to the electrochemically generated $MesNi^Ibpy$ complex

Substrate (RX)	$\frac{C_{RX}{}^0}{C^0{}_{complex}}$	$I_p{}^k/I_p{}^d$	lg(χ*k*)	χ*k*	k_1 /L mol^{-1} s^{-1}
Pr^iI	1	1.82	1.31	20.12	3950
i-$C_5H_{11}I$	1	1.80	1.28	19.21	3800
PhI	1	1.77	1.24	17.51	3450
PhBr	1	1.52	0.15	1.41	280
	2	1.71	0.20	1.58	310
4-TolBr	1	1.42	−0.21	0.62	120
	2	1.55	−0.25	0.56	110
	5	1.81	−0.20	0.63	120
MesBr	1	1.25	−0.51	0.32	60
	2	1.35	−0.62	0.25	50
	5	1.62	−0.53	0.31	60
BuBr	1	1.27	−0.52	0.32	60
	2	1.41	−0.53	0.31	60
	5	1.64	−0.45	0.36	70
2-ClTh	1	1.62	0.53	3.16	620

We obtained the sequence of relative reactivity of the substrates: MesBr < BuBr < *o*-BrTol < PhBr < 2-ClTh < < PhI < *i*-$C_5H_{11}I$ < Pr^iI.

Thus, the use of the electrochemically synthesized model σ-MesNibpyBr aryl complex made it possible to determine the key stage of cross-coupling producing MesR, *viz.*, interaction of $MesNi^Ibpy$ with RX, and to estimate the rate constants of this reaction.

Experimental

A stationary disk glassy-carbon (GC) electrode with a surface area of 3.14 mm^2 was used as a working electrode in CV studies. Voltammograms were recorded using a PI-50-1 potentiostat with a PR-49 programmer and an electrochemical cell connected by the three-electrode scheme in DMF against the background of Et_4NBF_4 (0.1 mol L^{-1}) on a two coordinate recorder with a sweep rate of 50 mV s^{-1}. A reference electrode was Ag/0.01 *M* $AgNO_3$ in MeCN. A Pt wire 1 mm in diameter was used as auxiliary electrode. Measurements were carried out in an argon atmosphere in a cell thermostatted at 25 °C. A required amount of RX was added into a solution of the nickel complex (10^{-2} mol L^{-1}) using a 10-μL chromatographic syringe.

The $NiBr_2bpy$ complex was synthesized from $NiBr_2$ and 2,2´-bipyridine in EtOH with stirring for 5 h. The precipitate that formed was filtered off and dried in a desiccator at 30 °C for 24 h. Commercial organic halides (reagent grade) were purified by distillation to unchanged physical constants.

Processing of CV data. The error of results of measuring peak potentials was ≤10 mV. The number of electrons transferred from the electrode to the nickel complex was determined by comparison of the currents in the peaks of the compounds under study with the current of the first diffusion peak of benzophenone reduction (1e) under similar conditions.

Rate constants of oxidative addition (k_1) of organic halides to the organonickel σ-complex were calculated using a known procedure[4] from the calibrated curves for the excess factors $C_S{}^0/C_M{}^0$ (where $C_S{}^0$ is the volume concentration of the substrate, and $C_M{}^0$ is the volume concentration of the mediator) based on the plot of the ratio of the catalytic (kinetic) to diffusion currents $I_p{}^k/I_p{}^d$ *vs.* $\log\chi k$, where χk is the kinetic parameter equal to $k_1C_M{}^0RT/(FV)$.

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