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Electrochemical Reduction of Halopyridines Catalyzed by $Ni^0(bipy)_2$

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Abstract—The possibility of electrochemical reduction of halopyridines in the presence of $Ni^0(bipy)_2$ (bipy = 2,2'-bipyridine) was shown, and the features of homo- and cross-coupling with participation of PyX (Py = 2- or 3-pyridyl, X = Cl, Br) were studied.

Formation of pyridines with functional substituents by replacement of halogen in the C–Hal bond by the pyridine fragment receives a particular attention. At the same time, electrochemical studies in this direction are scarce [1–3]. Thus, it is urgent to examine the possibility of electrochemical reduction of halopyridines catalyzed with an Ni^0 complex and the features of homo- and cross-coupling with participation of PyX (Py = 2- or 3-pyridyl, X = Cl, Br). The catalytic cycle of reduction of organic halides in the presence of electrochemically generated complexes Ni^0L_n (L = π-acceptor ligand) involves the stages of the oxidative addition to the catalyst and reductive elimination of σ organic complexes of nickel.

As catalyst precursors $Ni(bipy)_3(BF_4)_2$ and $NiBr_2(bipy)$ (bipy = 2,2'-bipyridine) can be used. The voltammetric studies of the catalytic properties of these complexes with various numbers of ligands show that the catalyst activity during oxidative addition depends on the number of ligands. Different coordination numbers typical for nickel in various oxidation states determine the loss of one bipy ligand in the course of reduction [scheme (1)]. For $Ni(bipy)_3(BF_4)_2$ in the presence of chloropyridines we observed no catalytic increase in the current at the potentials of Ni^{II} reduction wave (≤6%, which is close to the experimental error), with significant decrease in the Ni^0 oxidation current (Figs. 1 and 2, curves *2*). In both cases the rate constant k_0 of the oxidative addition of PyCl to the reduced species $Ni^0(bipy)_2$ [scheme (2)] can be calculated from the relative changes of the anodic current I_a/I_c at various scanning rates of potential and large excess of substrate (Table 1) [4]:

$$Ni^{2+}(bipy)_3 + 2e \rightleftarrows Ni^0(bipy)_2 + bipy, \qquad (1)$$

$$Ni^0(bipy)_2 + PyCl \xrightarrow{k_0} PyNiCl(bipy)_2. \qquad (2)$$

The rate constant k_0 of oxidative addition for 3-ClPy is higher than for 2-ClPy; for $NiBr_2(bipy)$ it is higher than for $Ni(bipy)_3(BF_4)_2$. In all the tests, with addition of bromopyridines to the solutions of nickel complexes the catalytic increase in the current due to the regeneration of Ni^0 catalyst [e.g., reactions (3–7)] is observed. As a result, direct calculation of k_0 by common methods is impossible.

Table 1. Rate constants of oxidative addition of PyX to Ni^0 (k_0, $mol^{-1}\ l^{-1}\ s^{-1}$, procedure [4]) and rate constants of catalyst regeneration (k_{ap}, $mol^{-1}\ l^{-1}\ s^{-1}$, procedure [5]) [c(PyX) 0.126 M]

Complex	PyX	$(I_p - I_n)/I_n$,[a] %	k_0	k_{ap}	Complex	PyX	$(I_p - I_n)/I_n$,[a] %	k_0	k_{ap}
$Ni^{2+}(bipy)_3(BF_4)_2$	2-ClPy	6	10	–	$Ni^{2+}Br_2(bipy)$	2-BrPy	110	–	35
	3-ClPy	6	22	–		3-ClPy	3	83	–
	2-BrPy	100	–	30		3-BrPy	33	–	–
	3-BrPy	43	–	13					

[a] I_p and I_n are the reduction currents of complex in the presence and absence of the substrate.

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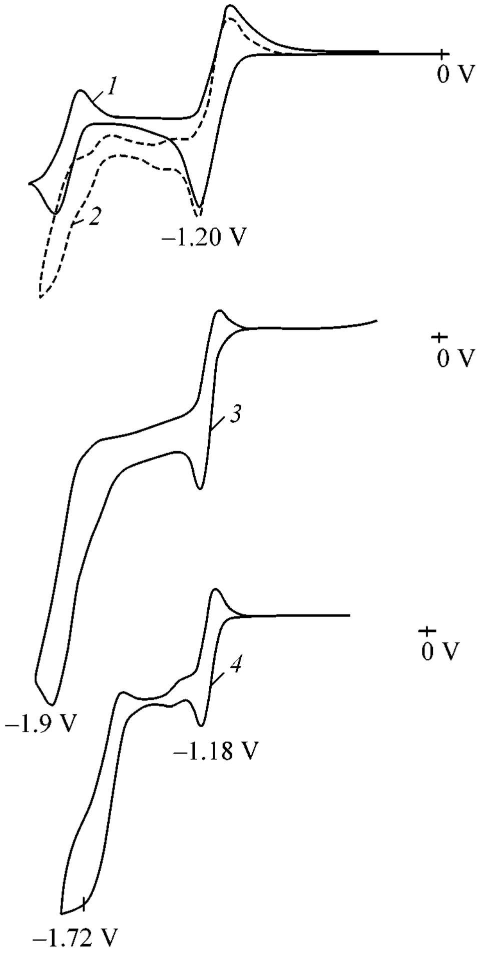


Fig. 1. Voltammograms of $Ni^{2+}(bipy)_3(BF_4)_2$ (*c* 0.017 M) in the (*1*) absence and (*2*) presence of 2-ClPy (*c* 0.085 M), (*3*) after passing of 2e per nickel(II) complex at –1.2 V, and (*4*) after passing of 5.2e per nickel(II) complex in the absence of 2-ClPy (vs. saturated calomel electrode).

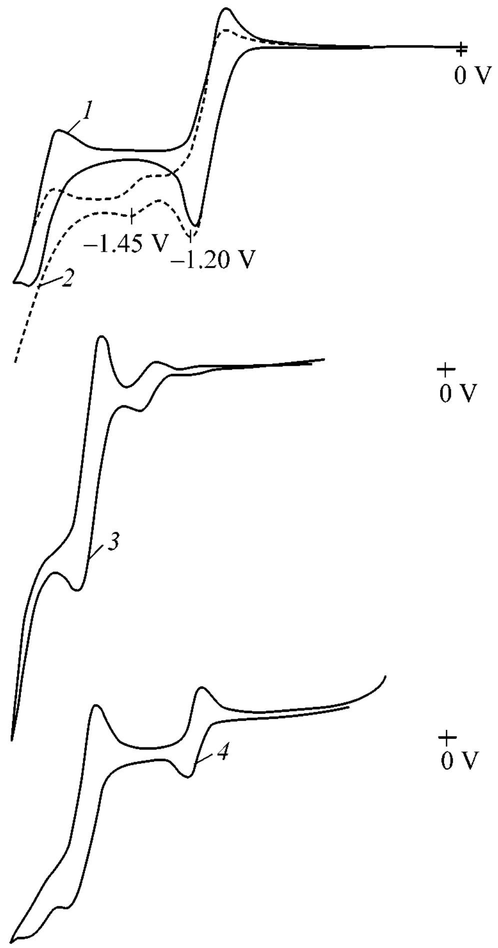


Fig. 2. Voltammograms of $Ni^{2+}(bipy)_3(BF_4)_2$ (*c* 0.017 M) in the (*1*) absence and (*2*) presence of 3-ClPy (*c* 0.17 M), (*3*) after passing of 8e per nickel(II) complex at the potential from –1.20 to –1.25 V ($I \to 0$), and (*4*) after passing of 16e per nickel(II) complex at –1.4 V.

At the same time, at significant current increase the apparent rate constant of catalyst regeneration can be determined using the Saveant procedure [5]. The rate constant of pseudo-first-order reduction of 2-BrPy is close for both catalysts.

$$\longrightarrow Ni^0(bipy)_2 + PyBr \xrightarrow{k_0} PyNiBr(bipy)_2 \qquad (3)$$

$$Ni^0(bipy)_2 + PyNiBr(bipy)_2 \rightarrow PyNi^{1+}(bipy)_2 + Ni^{1+}Br(bipy)_2 \qquad (4)$$

$$PyNi^{1+}(bipy)_2 + PyBr \rightarrow Py_2Ni^{3+}Br(bipy)_2 \qquad (5)$$

$$Py_2Ni^{3+}Br(bipy) \rightarrow \text{Reaction products} + Ni^{1+}Br(bipy) \qquad (6)$$

$$Ni^{1+}Br(bipy)_2 + e \rightleftarrows Ni^0(bipy)_2 + Br^- \qquad (7)$$

In some experiments the increase in the current of reduction of $Ni^0(bipy)$ to $Ni^0(bipy)^{\dot{-}}$ at a potential of –1.9 V vs. saturated calomel electrode is observed. In this case we can calculate the apparent rate constant of regeneration of the catalyst, which acts as an electron-transfer agent similar in properties to the outer-spherical radical anion (Table 2). This procedure is correct

Table 2. Apparent rate constants of regeneration of $Ni^0(bipy)^{\dot{-}}$ catalyst in the presence of halopyridines in DMF [$c(Ni^{2+}Br_2(bipy))$ 1.7×10^{-2} M]

PyX	$I_p/I_n[Ni(0)/Ni(0)^{\dot{-}}]$	*c*(PyX), M	k_{ap}, $mol^{-1}\,l^{-1}\,s^{-1}$
3-ClPy	7.0	0.34	116
3-BrPy	8.0	0.085	604
2-ClPy	5.5	0.085	308

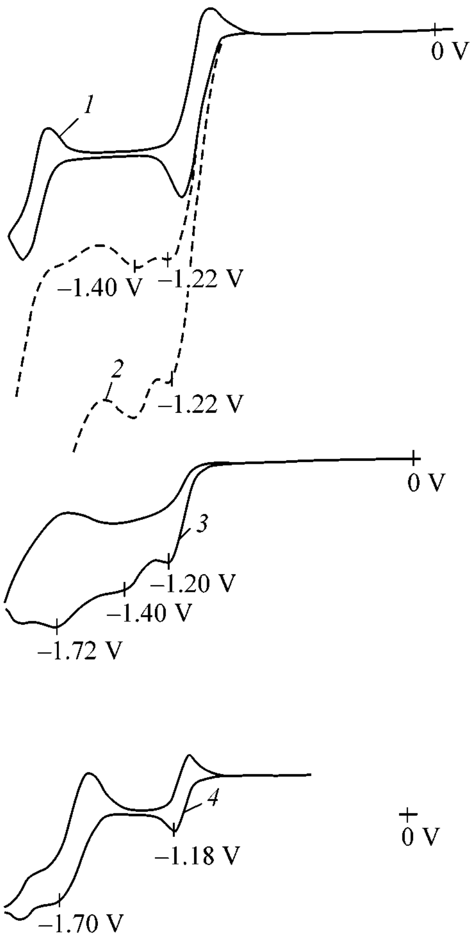


Fig. 3. Voltammograms of $Ni^{2+}(bipy)_3(BF_4)_2$ (*c* 0.017 M) in the (*1*) absence and (*2*) presence of 2-BrPy (*c* 0.034 and 0.085 M), (*3*) after passing of 2.2e per nickel(II) complex at –1.20 V, and (*4*) after passing of 3.9e per nickel(II) complex at –1.2 V ($I \rightarrow 0$).

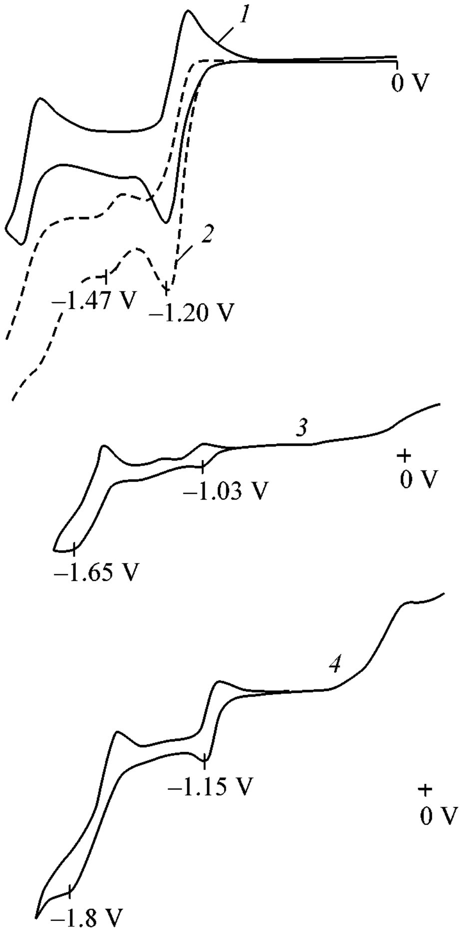


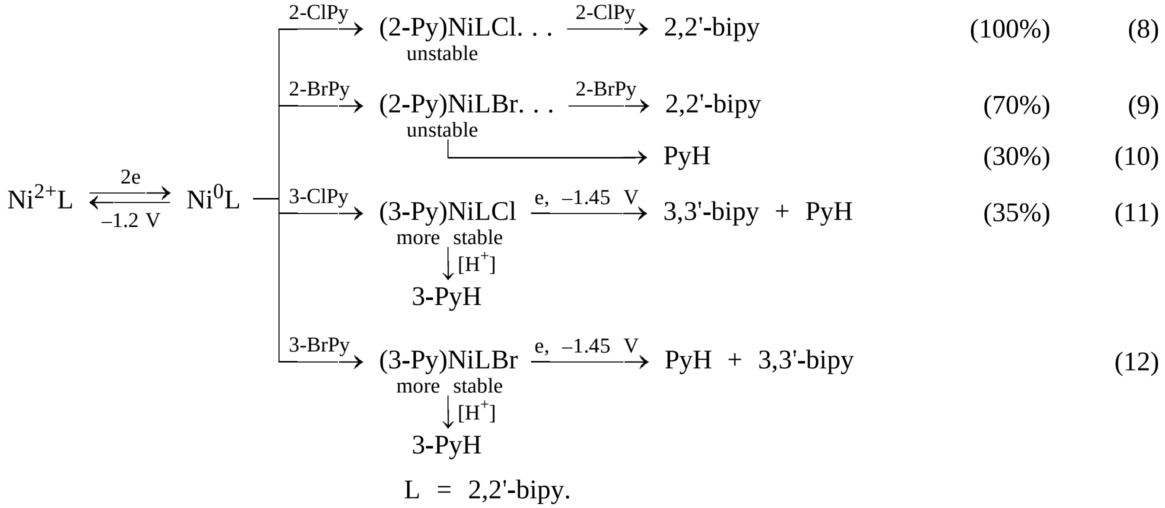
Fig. 4. Voltammograms of $Ni^{2+}(bipy)_3(BF_4)_2$ (*c* 0.017 M) in the (*1*) absence and (*2*) presence of 3-BrPy (*c* 0.085 M), (*3*) after passing of 2e per nickel(II) complex at –1.27 V ($I \rightarrow 0$), and (*4*) after passing of 4e per nickel(II) complex at –1.7 V.

only if the rate of reaction of PyX with Ni^0 forming at the first-wave potentials is relatively small and no waves of the reaction products and no current increases are registered in the voltammograms, i.e., Ni^0 is stable under the experimental conditions and the rate of its reaction with PyX is negligible. For example, such calculations are incorrect for the reaction with 2-BrPy.

We found that $ArNi^+(bipy)$ reacts with all halopyridines; however, in the case of preliminary mixing of aryl halides (1 : 1 molar ratio) the cross-coupling with 3-bromopyridine during electrolysis is insignificant [6].

We studied voltammograms of nickel complexes with bipy in the presence and absence of various halopyridines. In the presence of 2- and 3-ClPy the Ni^{II}/Ni^0 wave remains almost constant, whereas the reaction with 3-ClPy is more rapid than with 2-ClPy (k_0 22 and 10 $mol^{-1}\,l^{-1}\,s^{-1}$, respectively) for $Ni(bipy)_3(BF_4)_2$ and more rapid as compared with 2-BrTol. As shown previously, the reaction with chloropyridine is unfavorable for cross-coupling. In the case of bromopyridines [reactions (9) and (12)] the current of Ni^{II} reduction at –1.2 V increases owing to the catalyst regeneration, and thus evaluation of k_0 is impossible.

Now, let us analyze the reduction products of halopyridines in the presence of $Ni^0(bipy)_2$ catalyst and evolution of voltammograms in the course of electrolysis. During electrolysis of 2-ClPy of 2-BrPy in the presence of $Ni(bipy)_3(BF_4)_2$ (Figs. 1–4) rapid regeneration of the catalyst at –1.2 V proceeds, and the main product of the process is 2,2'-bipy (100% for 2-ClPy and 70% for 2-BrPy). During electrolysis of 3-ClPy or 3-BrPy nickel is gradually bound in the σ complex $PyNi^{2+}X(bipy)$, and the catalyst is



blocked. Small amounts of 3,3'-bipy (35%) are formed in reaction with 3-ClPy and only at more negative potentials (–1.48 and –1.7 V), and in the case of 3-BrPy [reactions (11) and (12)] this reaction does not proceed at all.

As a result, the reaction of Ni^0 with halopyridines is unfavorable for cross-coupling, because the catalyst is consumed in the reaction and almost no product is formed.

Our tests showed that electrochemically generated complexes $Ni^0(bipy)_n$ are the effective catalysts for dehalogenation of halopyridines, and the reactions products are the corresponding bipyridines (from 2-ClPy), pyridine (from 3-ClPy), or their mixture. The reaction of $Ni^0(bipy)_n$ with PyX yields σ-pyridyl complexes of nickel, which do not react with the other organic halides RX and thus do not yield the cross-coupling products:

$$Ni^0L + PyX \xrightarrow{k_0} PyNi^{2+}LX, \quad (13)$$

for 2-X:

$$PyNi^{2+}LX + Ni^0 \rightarrow PyNi^{1+}L + X^- \ (-1.2\ B), \quad (14)$$

for 3-X:

$$PyNi^{2+}LX + e \rightarrow PyNi^{1+}L + X^- \ (-1.45\ B), \quad (15)$$

$$PyNi^{1+}L + PyX \rightarrow Py_2Ni^{3+}LX \rightarrow Py_2 + Ni^{1+}LX. \quad (16)$$

EXPERIMENTAL

The kinetic characteristics of the process were studied using voltammograms registered for each substrate–metal complex system. $Ni^{2+}Br_2(bipy)$ was prepared from $Ni^{2+}Br_2 \cdot 3H_2O$ and 1 equivalent of 2,2'-bipyridine, and $Ni^{2+}(bipy)_3(BF_4)_2$, from $Ni(BF_4)_2 \cdot 6H_2O$ and 3 equivalents of 2,2'-bipyridine in ethanol. The solutions were stored for 12 h. The precipitate was filtered off, washed with ethanol, and dried in a vacuum at 70°C for 24 h. The saturated calomel reference electrode was placed into the compartment filled with DMF and Bu_4NBF_4 separated from the solution with a glass membrane. The working electrode was a gold disc 0.25 mm in diameter. For the preparative electrolyses a cylindrical nickel gauze cathode was used. The solvents and supporting electrolyte (Bu_4NBF_4) were purified by the standard procedures [7]. The chromatographic analysis of the reaction mixtures and products was performed on a Chrom-4 gas–liquid chromatograph [glass columns packed with Chromaton N-AW, 5% Silicone SE-30 (0.125–0.160 mm)] equipped with a flame-ionization detector.

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