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Electrocatalytic reactions involving the Ni^{II}—Zn^{II}—2,2´-bipyridine system

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Factors determining the effect of Zn^{II} ions on the catalytic activity of the Ni^{II} complexes with 2,2´-bipyridine (bpy) in the reduction of organohalides were elucidated by cyclic voltammetry and electrolysis. The mechanism proposed involves the reduction of the Ni^{II}bpy complex to Ni^{0}bpy, the oxidative addition of organohalides to the Ni^{0}bpy complex, and nickel transmetallation with the cathode-generated Zn^{0} to form an organozinc compound.

Key words: zinc ions, nickel complexes, 2,2´-bipyridine, electrochemical catalysis, cyclic voltammetry.

Indirect reduction and oxidation of organic compounds through the formation and regeneration of redox reactants at an electrode, has acquired increasing importance among modern methods of organic synthesis.[1]

Nickel complexes are widely used as catalysts in the electrochemical reduction of organohalides. For instance, a nickel(II) complex with 2,2´-bipyridine (bpy), Ni^{II}bpy, is an efficient catalyst[2,3] for homo- and cross-coupling of organohalides, the addition of organohalides to carbonyl compounds,[4,5] the synthesis of triorganylphosphines from organohalides and chlorophosphines,[6—8] and electrochemical arylation and alkylation of white phosphorus.[9,10] However, the key stages of the mechanisms of the reactions catalyzed by Ni^{0} complexes were sometimes postulated without corresponding substantiation.

One of the problems in studies of homogeneous processes catalyzed by transition metal complexes is to elucidate the nature and mechanisms of synergistic effects of various metal ions in electrolytes. Previously,[11—13] it was repeatedly pointed out that the nature of sacrificial anodes (and, hence, of the metal ions generated in their dissolution) determines the pathways of transformations of substrates, product yields, and the kinetics of the process if the reaction is carried out without separation of the anodic and cathodic compartments. In particular, electrochemical cross-coupling of allyl halides or α-haloethers with aromatic carboxylates using Mg or Al anodes is characterized by low selectivity. In the case of Zn anode, the target products are formed[13,14] in quantitative yields. The mechanism of the overall process and the key stage of transmetallation have not been well substantiated as yet.

The main goal of this work was to study the effect of zinc(II) ions on the kinetics and transformation pathways of organohalides under conditions of homogeneous electrochemical catalysis by the Ni/Zn/bpy system and to elucidate the transmetallation mechanism.

Experimental

Cyclic voltammetry (CV) studies were carried out using a PI-50-1 potentiostat attached to an XY-recorder, a PR-49 programmer, and the electrochemical cell placed in the circuit in three-electrode connection. The rate of linear potential sweep was 50 mV s^{-1}. The working electrode was a stationary glassy-carbon disk electrode with a working surface area of 3.14 mm^2, the auxiliary electrode was a Pt wire, and the reference electrode was the Ag/0.01 *M* $AgNO_3$ system in MeCN. Measurements were carried out in DMF using a thermostatted cell (25 °C) under an argon atmosphere. The number of electrons (n) participating in the electrochemical reaction was calculated with respect to benzophenone used as a reference (the peak current was 30 μA at a concentration of 10^{-2} mol L^{-1}). The apparent rate constant for catalyst regeneration (K_{app}) was calculated following the known procedure.[6]

Electrolysis was performed in the three-electrode cell of volume 40 mL using a B5-49 DC power supply. The potential of the working electrode was set using a Shch50-1 voltmeter *vs.* the reference electrode (Ag/0.01 *M* $AgNO_3$ in MeCN). The working surface area of a cylindrical Pt-cathode was 20 cm^2. A Mg rod was used as anode. Its working surface was thoroughly conditioned by grinding with emery cloth before electrolysis. During electrolysis the electrolyte was stirred with a magnetic stirrer at constant argon flow.

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The reaction mixtures and products were analyzed by GLC on a "Chrom-5" chromatograph (with catharometer as detector, He as the carrier gas, glass columns 120×0.3 cm, 5% Silicon SE-30 (0.125—0.160 mm), and Chromaton N-AW).

N,*N*-Dimethylformamide was distilled by triple fractionation over calcinated potassium carbonate and molecular sieves (content of residual water was 0.010 to 0.005% by mass). Compounds used as background salts (Et_4NBr and Et_4NBF_4) were recrystallized twice from MeCN (Et_4NBr) and EtOH (Et_4NBF_4) and dried *in vacuo* at 100 °C for 48 h.

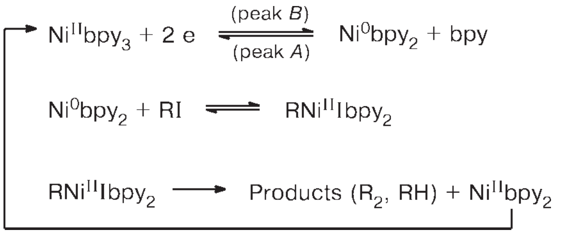
Compounds $NiCl_2bpy$, $NiBr_2bpy$, and $Ni(BF_4)_2bpy_3$ were obtained following the known procedure.[15]

Organohalides of "chemically pure" grade were purified by distillation until constant values of physical constants.

Results and Discussion

The addition of organohalides (RX) to a solution containing $Ni^{II}bpy_3$ causes a noticeable change in the shape of the CV curve. An increase in the reduction current of $Ni^{II}bpy_3$ allows one to assess the regeneration rate of the complex. In particular, the addition of Pr^iI or i-$C_5H_{11}I$ leads to an increase in the height of the cathodic peak (the catalytic current is denoted as I_{cat}), while its anodic response at the back scan of the CV curve disappears (Table 1, Fig. 1). This indicates a rather fast regeneration of the starting complex, accompanied by the formation of dehalogenation products of substrates added (Scheme 1).

Scheme 1



However, the presence of PhI, PhBr, and 2-BrTol has no effect on the height of the reduction peak of the Ni complex, which indicates that no fast interaction between Ni^0bpy_2 and these compounds occurs under these conditions.

Table 1. Characteristics of anodic and cathodic peaks in the CV curves for $NiCl_2bpy$ solution (10^{-2} mol L^{-1}) in the absence and in the presence of i-$C_5H_{11}I$ (10^{-2} mol L^{-1})

Solution composition	Peak	E_p/V	I_p/μA	*n*
$Ni^{II}bpy$*	*B*	−1.52	57	1.9
	A	−1.38	40	—
$Ni^{II}bpy + i$-$C_5H_{11}I$	*B′*	−1.52	90	3

Note. Here and in Tables 3—5 E_p is the peak potential, I_p is the height of anodic or cathodic peak, and *n* is the number of electrons participating in the process.

* $I_p{}^a/I_p{}^c = 0.67$ is the height ratio of anodic and cathodic peaks.

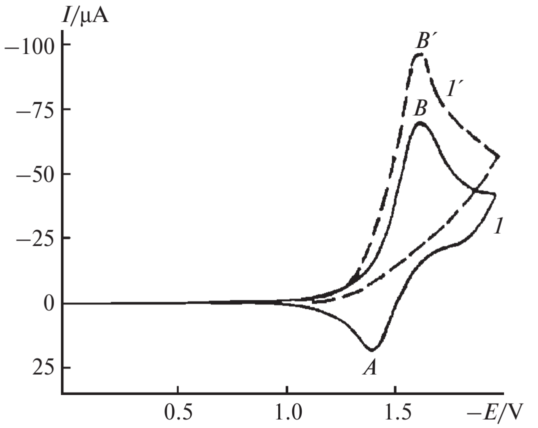


Fig. 1. CV curves for $NiCl_2bpy$ solution (10^{-2} mol L^{-1}) in the absence (*1*) and in the presence (*1′*) of i-$C_5H_{11}I$ (10^{-2} mol L^{-1}).

The catalytic-to-diffusion current ratio, I_{Cat}/I_D, plotted as function of the RX concentration is a straight line parallel to the abscissa axis for RX = PhI (Fig. 2, line *1*) and is a curve with saturation for 2-Brpy and i-$C_5H_{11}I$ (see Fig. 2, curves *2* and *3*, respectively). The latter points to fast regeneration of the catalyst at a potential equal to its reduction potential in the presence of 2-Brpy and i-$C_5H_{11}I$. The addition of Zn salt to a solution or the use of a Zn-anode is known[11] to be responsible for substantial changes in the rate and selectivity of reactions and in the product yields.

The apparent rate constants, K_{app}, for regeneration of the $Ni^{II}bpy$ catalyst in the absence and in the presence of Zn^{II} in the dehalogenation reactions under study are listed in Table 2. The K_{app} constant depends on the substrate concentration in a complex manner, which implies a com-

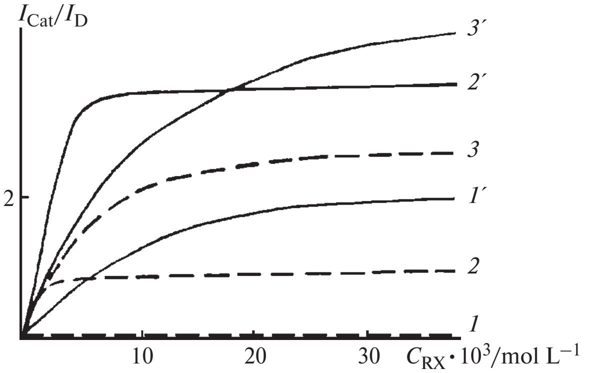


Fig. 2. The catalytic-to-diffusion current ratio (I_{Cat}/I_D) for reduction of $NiCl_2bpy$ (10^{-2} mol L^{-1}) plotted as function of the concentration of substrate RX (C_{RX}) in the absence (*1—3*) and in the presence (*1′—3′*) of $ZnCl_2$ (10^{-2} mol L^{-1}): PhI (*1*, *1′*); 2-Brpy (*2*, *2′*); and i-$C_5H_{11}I$ (*3*, *3′*).

Table 2. Apparent rate constants (K_{app}) for regeneration of the catalyst, Ni^{II}bpy (10^{-2} mol L^{-1}), in the absence and in the presence of $ZnCl_2$ (10^{-2} mol L^{-1})

Substrate (RX)	[RX]/mol L^{-1}	$K_{app} \cdot 10^{-2}$/mol^{-1} L^{-1} s^{-1}	
		Ni^{II}bpy	Ni^{II}bpy + Zn^{II}
PhI	$5 \cdot 10^{-3}$	—	2.8
	$1 \cdot 10^{-2}$	—	1.8
	$2 \cdot 10^{-2}$	—	1.2
	$3 \cdot 10^{-2}$	—	0.9
i-$C_5H_{11}I$	$5 \cdot 10^{-3}$	3.8	5.2
	$1 \cdot 10^{-2}$	2.7	3.6
	$2 \cdot 10^{-2}$	1.9	2.6
	$3 \cdot 10^{-2}$	—	2.0
2-Brpy	$5 \cdot 10^{-3}$	3.4	10.8
	$1 \cdot 10^{-2}$	2.3	9.1
	$2 \cdot 10^{-2}$	—	4.8

plex sequence of individual stages, differing from conventional catalytic ECE-sequence. Therefore, we considered the complex Ni/Zn/bpy system as consisting of some components and studied the reduction of Zn^{II} and Ni^{II} as individual processes, in combination, and in the presence of bpy and RX.

In the absence of a ligand, the CV curves for Zn^{II} (anhydrous $ZnCl_2$ was added) measured with Et_4NBF_4 as the background electrolyte exhibit one cathodic peak *A* ($E_p = -1.72$ V) and two anodic peaks at $E_p = -0.78$ V (*B*) and $E_p = -1.24$ V (*C*) (Table 3, Fig. 3). All the peaks are symmetrical and have no diffusion tails, which is characteristic of adsorption peaks. Probably, they correspond to the electrochemical oxidation of Zn^0; however, elucidation of their nature is beyond the scope of this work. The addition of bpy (at Zn^{II} : bpy = 1 : 1 mole ratio) leads to an increase in the height of the reduction peak of Zn^{II} (*D*) in the CV curve; a new anodic peak (*E*) related to peak *D* appears simultaneously, whereas both adsorption peaks (*B* and *C*) disappear. This points to transfer of the reduced zinc by 2,2´-bipyridine to the bulk of the solution. At more negative potentials, the second reversible peak, *F*, appears, which seems to correspond to the reduction of the Zn^0bpy complex (see Fig. 3, Table 3).

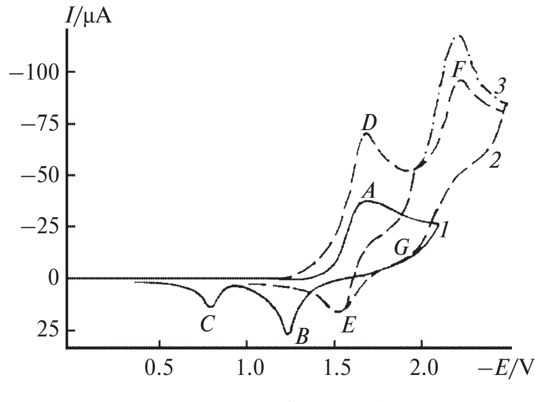


Fig. 3. CV curves for $ZnCl_2$ (10^{-2} mol L^{-1}) (*1*), $ZnCl_2$: bpy = 1 : 1 (*2*), and $ZnCl_2$: bpy = 1 : 3 (*3*) solutions in DMF (with Et_4NBF_4 as supporting electrolyte).

Table 3. Characteristics of cathodic and anodic peaks in the CV curves for $ZnCl_2$ solution (10^{-2} mol L^{-1}) in the absence and in the presence of bpy

Solution composition	Peak	E_p/V	I_p/μA	*n*
Zn^{II}	*A*	−1.72	34	1.1
	B	−1.24	25	—
	C	−0.78	10	—
Zn^{II} + bpy	*D* *	−1.72	50	1.7
(1 : 1)	*E* *	−1.55	30	1.0
	F **	−2.20	35	1.2
	G **	−1.95	30	1.0

Note. For notations, see Note to Table 1.
* $I_p^a/I_p^c = 0.6$. ** $I_p^a/I_p^c = 0.86$.

The CV curves for Zn^{II} measured in the presence of increasing RX concentrations (in particular, PhI) exhibit a decrease in the intensity and further disappearance of the anodic oxidation peaks of metallic Zn, whereas the cathodic peak remains unchanged (Fig. 4). In this case, we suggest the formation of the known**16** compound PhZnI in the reaction of PhI with Zn^0 that was electrochemically precipitated at the cathode or with such an intermediate as Zn^I:

$$Zn^0\ (Zn^I) + PhI \longrightarrow PhZnI.$$

The addition of PhI to the solution of the Zn^{II}bpy complex has little effect on the shape of the CV curves (Fig. 5). Only a slight increase in the current of the second cathodic peak is observed, followed by disappearance of the anodic responses of both cathodic peaks in the back scan at rather high concentrations of PhI (see Fig. 5).

Hence, complex Zn^0bpy is less reactive toward PhI than Ni^0bpy.

When Ni^{II}, Zn^{II}, and bpy are simultaneously present in solution, the CV curves exhibit two cathodic peaks, *A* and *B*, corresponding to the reduction of the nickel (Ni^{II}/Ni^0) and zinc (Zn^{II}/Zn^0) complexes (Table 4,

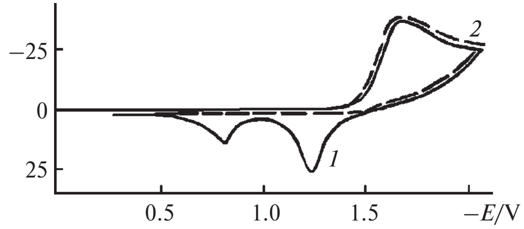


Fig. 4. CV curves for $ZnCl_2$ solutions (10^{-2} mol L^{-1}) in DMF in the absence (*1*) and in the presence (*2*) of PhI (10^{-2} mol L^{-1}).

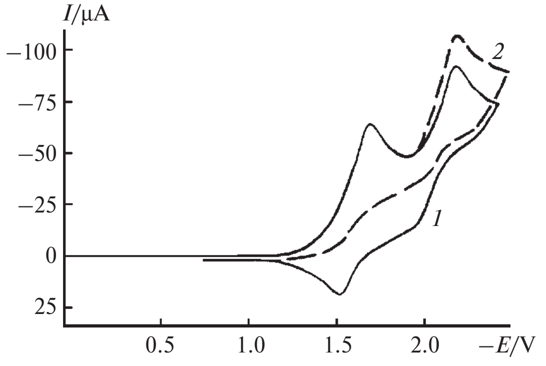


Fig. 5. CV curves for $ZnCl_2$/bpy solutions (10^{-2} M) in DMF in the absence (*1*) and in the presence (*2*) of PhI (10^{-2} mol L^{-1}).

Table 4. Characteristics of cathodic and anodic peaks in the CV curves for $NiCl_2bpy$ (10^{-2} mol L^{-1})/$ZnCl_2$ (10^{-1} mol L^{-1}) solution in DMF in the presence of i-$C_5H_{11}I$ (10^{-2} mol L^{-1}) and PhI (10^{-2} mol L^{-1})

Solution composition	Peak	E_p/V	I_p/μA	*n*
$Ni^{II}bpy + Zn^{II}$	*A**	−1.52	80	2.7
	*A′**	−1.38	60	2.0
	*B***	−1.72	100	3.3
	*B′***	−1.60	80	2.7
$Ni^{II}bpy + Zn^{II}$ + + i-$C_5H_{11}I$	*C*	−1.52	140	4.7
	D	−1.72	100	3.3
$Ni^{II}bpy + Zn^{II}$ + + PhI	*E*	−1.52	118	3.9
	F	−1.72	100	3.3

Note. For notations, see Note to Table 1.
* $I_p^a/I_p^c = 0.75$.
** $I_p^a/I_p^c = 0.8$.

Fig. 6). The presence of anodic responses of these peaks (*A′* and *B′*) indicates that reduction results in the formation of Ni^0bpy and Zn^0bpy complexes that are stable in the solution. The addition of organohalides RX to the solution leads to a substantial catalytic increase in the current of the reduction peaks of $Ni^{II}bpy$ (*C* and *E*) even for such a substrate as PhI (peak *E*), which causes no regeneration of the electrochemically active form of the Ni complex at this potential in the absence of Zn salt (see Fig. 2).

The I_{Cat}/I_D ratio plotted as function of the RX concentration in the presence of ten-fold excess of $ZnCl_2$ represents a curve with saturation, and the catalytic effect (I_{Cat}/I_D) is much more pronounced than in the absence of $ZnCl_2$ (see Fig. 2, curves *1′—3′*). The K_{app} values for regeneration of the catalyst become 1.5 to 3 times higher (see Table 2).

To account for this effect, let us consider two reasons: first, a decrease in the coordinative satutation and, correspondingly, an increase in the reactivity of the Ni^0 complex and, second, the appearance in the system of the active form of zinc, Zn^0 (or, partially, Zn^0bpy), involved in the regeneration of the catalyst. A decrease in the bpy concentration in the solution below the Ni : bpy = 1 : 1 ratio in the presence of PhI and i-$C_5H_{11}I$ causes no additional catalytic effect. Taking into account also the higher stability of the Ni—bpy complex compared to the Zn—bpy complex, the first reason should be ignored. Therefore, we believe that the most plausible reason for the synergistic effect of the Zn additive is the occurrence of exchange reactions, or transmetallation.

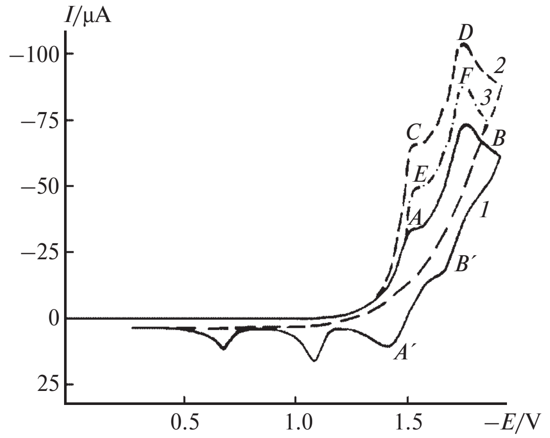


Fig. 6. CV curves for $NiCl_2bpy$ (10^{-2} mol L^{-1})/$ZnCl_2$ (10^{-1} mol L^{-1}) solutions (*1*) in the presence of i-$C_5H_{11}I$ (10^{-2} mol L^{-1}) (*2*) and PhI (10^{-2} mol L^{-1}) (*3*).

Previously,[13,14] transmetallation of Ni complexes in the presence of Zn^{II} resulting in organozinc intermediate was studied:

$$RNi^{II}X + Zn^{II} \longrightarrow RZn^{II}X + Ni^{II}. \qquad (1)$$

It was shown that electrochemical coupling of aromatic halides containing acceptor groups in the aromatic ring requires the presence of Zn^{2+} ions in solution or the use of a Zn-anode (Mg-anodes are inactive in this process). However, no evidence for transmetallation following route (1) is available in the literature. Moreover, from consideration of the series of thermodynamic redox potentials it follows that this process is impossible since the ion of a more active metal (Zn^{II}) cannot displace the ion of the less active metal (Ni^{II}) in an aqueous medium. Since Ni^{II} is also reduced in DMF at lower potentials than Zn^{II}, one can suggest that the order of the redox potentials remains unchanged.

GLC study of the electrolyte after the electrolysis of PhI (or PhBr) in the presence of $NiBr_2bpy$ and $ZnBr_2$ (mole ratio was 6 : 1 : 10) revealed the presence of benzene. However, no diphenyl (product of homo-coupling of PhI) was found even as traces. Diphenyl is the main product of electrolysis in the presence of $Ni^{II}bpy$ and in the absence Zn^{II}. One can assume that benzene is formed as a result of partial decomposition of PhZnI, the more so the acid hydrolysis of the electrolyte leads to a substantial increase in the amount of benzene found in the solution. The addition of saturated solution of I_2 in DMF to the electrolyte obtained after the electrochemical transformation of PhBr into PhZnBr leads to chromatographic detection of large amount of PhI formed by the PhZnBr oxidation.

Therefore, catalytic amounts of the Ni—bpy complex allow the transformation of PhBr into PhZnBr. To elucidate the transformation pathways of the intermediate organonickel into organozinc compounds, we used a model compound, namely, the σ-complex *o*-tolylnickel(2,2´-bipyridine) bromide (*o*-TolNiBrbpy), obtained by two-electron reduction of $NiBr_2$bpy in the presence of *o*-BrTol (1 : 2) (Q = 2 F per mole Ni^{II}). This bromide is rather stable in solution due to the presence of a Me group in the *ortho*-position of benzene ring and is a convenient model for studying various reactions of σ-complexes[17—19] under conditions of electrocatalysis. We found that the reduction peak of *o*-TolNiBrbpy remains unaffected upon the addition of excess $ZnBr_2$ (up to 10-fold) to the solution of *o*-TolNiBrbpy in DMF (Fig. 7). Therefore, one can assume that in this case reaction (1) proceeds slowly or does not proceed at all.

The formation of organozinc compounds under conditions of electrolysis is based on the assumption of the appearance of Zn^0 (or, partially, Zn^0bpy) in the intermediate stages of the process. In this case, a reductive substitution reaction can proceed

$$\mathrm{RNi^{II}X + Zn^0 \longrightarrow RZn^{II}X + Ni^0.} \qquad (2)$$

The reduction potential of Zn^{II} is only 200 mV more negative than that of Ni^{II}. This allows the formation of Zn^0 immediately at the electrode (a general scheme of the process can be represented by reactions (3)—(7); reaction (5) describes the formation of Zn^0) under conditions of galvanostatic electrolysis. In addition, the reduction of $ZnCl_2$ in the bulk by the electrochemically generated Ni^0bpy complex following reaction (7) is possible. Due to a large deficiency of the bpy ligand in the system and lower stability of its Zn-complex compared to the Ni-complex, the concentration of bound Zn^0bpy is low and the determining role in the catalytic cycle is played by Zn^0, which can replace the Ni atom in the organonickel compound according to reaction (6).

$$\mathrm{Ni^{II}bpy + 2\,e \rightleftharpoons Ni^0bpy} \qquad (3)$$

$$\mathrm{Ni^0bpy + RX \rightleftharpoons RNi^{II}Xbpy} \qquad (4)$$

$$\mathrm{Zn^{II} + 2\,e \longrightarrow Zn^0}$$

$$\mathrm{or\ Zn^{II} + bpy + 2\,e \longrightarrow Zn^0bpy} \qquad (5)$$

$$\mathrm{Zn^0 + RNi^{II}Xbpy \longrightarrow RZn^{II}X + Ni^0bpy} \qquad (6)$$

$$\mathrm{Ni^0bpy + Zn^{II} \longrightarrow Ni^{II}bpy + Zn^0} \qquad (7)$$

Catalytic increase in the reduction current of Ni^{II}bpy is due to the regeneration of this compound. According to this scheme, Zn^{II} and RX are reduced concurrently. The final product of the transformation of RX (RZnX) is accumulated in the solution. The possibility for reaction (7) to proceed and the mechanism of mutual influence of the Ni and Zn compounds were confirmed by additional experiments.

We found that no Zn reduction peak appears in the CV curve upon the addition of increasing amounts of $ZnCl_2$ (up to the 1 : 3 ratio), though the intensity of the reduction peak of the complex increases (Table 5, Fig. 8). This suggests the occurrence of a catalytic process involving regeneration of the electrochemically active form of the Ni complex. In a simplified form this process can be represented as follows:

$$\mathrm{Ni^{II}bpy + 2\,e \rightleftharpoons Ni^0bpy,} \qquad (8)$$

$$\mathrm{Ni^0bpy + Zn^{II} \rightleftharpoons Ni^{II}bpy + Zn^0.} \qquad (9)$$

In Figure 8, two cathodic peaks (*D* and *E*) probably correspond to the reduction of the Zn^0—bpy and Ni^0—bpy complexes. If the [Zn] : [Ni] ratio is greater than 3 : 1, a reduction peak of Zn^{II} appears at $E = -1.72$ V in the mixture. It seems that the whole amount of Zn^{II} has no time to be transformed into Zn^0 by reaction (9).

Thus, the catalytic activity of the Ni—bpy complexes in the dehalogenation of RX enhances in the presence of the Zn^{II} ions generated during the dissolution of the anode or those added to the electrolyte. According to CV and electrolysis data, the key stage of the process is transmetallation of Ni^{II} in the RNi^{II}bpyCl complex by the electrochemically generated Zn^0 species.

Based on the results of our studies, we proposed a method for the electrochemical synthesis of some

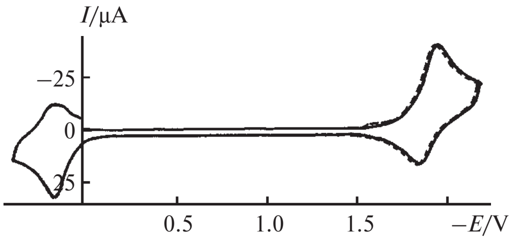


Fig. 7. CV curves for *o*-TolNiBrbpy solution (10^{-2} mol L^{-1}) in DMF in the absence (solid line) and in the presence (dashed line) of $ZnBr_2$ (10^{-1} mol L^{-1}).

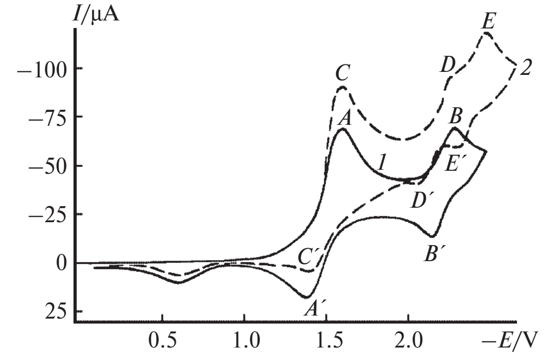


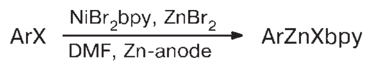
Fig. 8. CV curves for $NiCl_2bpy$ solution (10^{-2} mol L^{-1}) in DMF in the absence (*1*) and in the presence (*2*) of $ZnCl_2$ ($3 \cdot 10^{-2}$ mol L^{-1}).

Table 5. Characteristics of cathodic and anodic peaks in the CV curves for $NiCl_2bpy$ solution (10^{-2} mol L^{-1}) in DMF in the absence and in the presence of $ZnCl_2$ ($3 \cdot 10^{-2}$ mol L^{-1})

Solution composition	Peak	E_p/V	I_p/μA	I_p^a/I_p^c	n
$Ni^{II}bpy$	*A*	−1.52	57	0.67	1.9
	A′	−1.38	40		1.5
	B	−2.20	29	1.0	1.0
	B′	−1.95	28		0.9
$Ni^{II}bpy + Zn^{II}$	*C*	−1.52	80	0.5	2.7
	C′	−1.38	40		1.3
	D	−2.20	29	0.66	1.0
	D′	−1.95	23		0.8
	E	−2.45	20	0.75	0.7
	E′	−2.25	15		0.5

Note. For notations, see Note to Table 1.

organozinc σ-complexes according to the scheme shown below:



$$\mathrm{ArX} \xrightarrow[\text{DMF, Zn-anode}]{\text{NiBr}_2\text{bpy, ZnBr}_2} \mathrm{ArZnXbpy}$$

Stability of these complexes is determined by the nature of arylhalide.[14,20] The advantages of the method are mild reaction conditions, the absence of highly inflammable ether as solvent (one of the major obstacles to large-scale syntheses), and the possibility of varying the nature of the aromatic ring and substituents in the ring (*e.g.*, the use of aromatic halides with acceptor substituents). Organozinc compounds thus obtained can be used in various syntheses without their isolation from solution.[21] Preliminary results showed that the use of the Ni/Zn/bpy system allows one to obtain the highest yield of tertiary phosphines in the coupling reaction of organohalides with white phosphorus and to introduce the aromatic groups with acceptor substituents into various molecules in one stage, which cannot be done using conventional chemical methods.[6,18,21]

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