The role of Ni(0) complexes in electrochemical phosphorylation of organic halides
Part 1. Factors determining catalytic activity [1]

Yulia H. Budnikova [a], Yuri M. Kargin [b,*]

[a] Institute of Organic and Physical Chemistry of RAS, Arbuzov st., 8, Kazan, 420083, Russia
[b] Kazan State University, Lenin st., 18, Kazan, 420008, Russia

Abstract

The catalytic efficiency of Ni(0) complexes in coupling reactions of organic and organoelemental halides is shown to be determined by the degree of charge transfer, the value of the electrochemical gap, and the availability or absence of competitive redox reactions. © 1997 Elsevier Science S.A.

Keywords: Homogeneous redox catalysis; Ni(0) complexes; White phosphorus; Phosphorus chlorides; Electrochemistry

1. Introduction

The elaboration of highly selective reactions leading to formation of carbon–carbon and carbon–element bonds is amongst the most important problems in the rapidly expanding area of metallocomplex catalysis. Organic halide functionalization can be achieved by the use of some organometallic compounds; however, traditional chemical methods of catalyst regeneration are inconvenient because they demand stoichiometric amounts of reductants like zinc dust or Grignard reagents. Electrochemical methods for generation and regeneration of catalysts may work very productive in this respect, and in some instances one can obtain cross-coupling products from various halogen-containing compounds or mercaptans and to carboxylate arylhalides [1–6], and the like.

Presently, one of the most important problems is to elucidate the factors determining catalyst reactivity and their quantitative evaluation. However, the mechanism of these reactions is not absolutely clear, causing trouble in the choices of optimal conditions and catalyst.

We present here a brief overview of our recent work on electrochemical metallocomplex catalysis. We have succeeded in recent years in expanding the application area of familiar reactions of organic halide coupling on the basis of oxidative addition reactions. Thus, preliminary data show that one can perform phosphorylation of some organic halides under the action of electrochemically generated Ni complexes(0) with π-acceptor ligands using phosphorus chlorides [7,8] or white phosphorus as phosphorylating agents. Nickel complexes are very attractive catalysts because of their availability and ability to yield stable forms in low oxidation states (0, +1).

The main objective of this paper is to find factors determining the reactivity of Ni(0) complexes in oxidative addition reactions and to use the information obtained to make an informed choice of the catalyst when performing the synthesis on a large scale.

Among the other metals of the platinum group, nickel is noted for the least atomic size and d-orbital filling, resulting in a more effective display of electronic interactions between metal and ligand determining in many respects the catalytic ability of the complex. However, an analysis of the reduction process having regard to competitive homogeneous redox equilibria, limiting stages, calculation of rate and equilibrium constants is, in general, insufficient. Undoubtedly, a more comprehensive concept of the complex reduction mechanism, its redox properties and electron interactions between

---

* Corresponding author.
[1] To the memory of Professor Yu.T. Struchkov.

metal and ligand can be useful for evaluating the possible catalytic properties of intermediates with respect to different substrates. This paper presents our recent results on electrochemical reduction of organic and organoelemental halides under the action of Ni(0) complexes, the elucidation of the interrelation between the complex reduction mechanism, electron effects and ligand nature, and also some functions of the electrochemical potentials of complexes and substrates and complex catalytic activity in coupling reactions of C–Hal and E–Hal compounds. Attempts to elucidate the possibilities of phosphorylating organic halides electrochemically in the presence of chlorophosphines or white phosphorus under the action of Ni(0) complexes were also made. The electrochemical approach to using Ni(0) complex generation opens up some possibilities. Firstly, one can use catalytic rather stoichiometric amounts of complex which will be regenerated at the electrode and thereby reprocessing significant amounts of various substrates. Secondly, it is possible to evaluate quantitatively the rate of the catalytic reaction by electrochemical methods, and it was possible in some instances to divide an overall process into separate stages and to evaluate the reactivity of intermediates, and the stability of the metallocomplex in various forms.
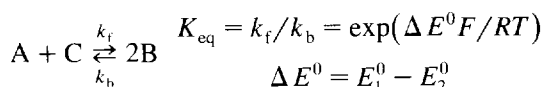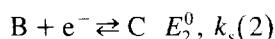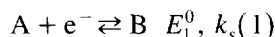
2. Results and discussion

2.1. Analysis of the mechanism of electrochemical reduction of Ni(II) complexes with π-acceptor ligands

The overall morphology of polarization reduction curves of Ni complexes with π-acceptor is rather diverse. This is not only because of the multistage character of the reduction process itself, but also due to the different experimental conditions used in various publications. According to the tasks of this investigation, we have believed that it would be profitable to perform a correlation analysis of the separate factors in the reduction mechanism and catalytic activity in similar conditions, whenever possible.

The reduction of Ni(II) complexes with such ligands as PPh_3, $(PhO)_3P$, $PhP(OBu)_2$, 2,2'-dipyridyl (dipy) and 1,10-phenanthroline (phen) at a glassy carbon electrode in acetonitrile with 0.1 M Et_4NBF_4 as supporting electrolyte is a two-electron process [1–9]. An appropriate peak of product oxidation in the cathodic process is observed during inverse scanning. This is evident from quantum-chemical concepts: the electron affinity in consecutive electron transfers to a molecule in the absence of profound chemical transformations is noticeably distinct, i.e. values of standard redox potentials for each subsequent stage became increasingly negative. Kinetic complications (overvoltage or charge transfer) can appear at each stage of electron transfer to some extent.

We use the approach elaborated in Ref. [10] in order to elucidate the most probable scheme of complex reduction. It is assumed that the two-electron process of initial complex reduction generally includes two stages of heterogeneous electron transfer and a homogeneous redox stage:

$$A + e^- \rightleftarrows B \quad E_1^0, \; k_s(1)$$

$$B + e^- \rightleftarrows C \quad E_2^0, \; k_s(2)$$

$$A + C \underset{k_b}{\overset{k_f}{\rightleftarrows}} 2B \quad \begin{array}{l} K_{eq} = k_f/k_b = \exp(\Delta E^0 F/RT) \\ \Delta E^0 = E_1^0 - E_2^0 \end{array}$$

The following parameters were chosen as diagnostic criteria: the ratio of the peak currents i_{pb}/i_{pf}, and the difference between the peak potentials $\Delta E^0 = E_{pb}^0 - E_{pf}^0$ on forward and reverse scans and its dependence on complex concentration and potential scan rate. It should be noted that, in chemical reactions, the complexes change conformation from an octahedron for Ni(II) to a tetrahedron for Ni(I) and Ni(0) and the reaction of ligand elimination under changes of metal oxidation state is also possible.

It was shown, as a result of these experiments [11], that the reduction process for Ni(II) complex with dipy included only two single-electron stages, and the stage of second electron transfer was the limiting one, whereas competitive stages were absent, $\Delta E^0 = -60$ to 70 mV. When the Ni(II) complex with phen is reduced, the process of first electron transfer is slowed down, $\Delta E^0 = -30$ to 60 mV, and redox reactions are also absent. In the case of reduction of Ni(II) complexes with phosphites, $(^iPrO)_3P$, $PhP(OBu)_2$, $(PhO)_3P$, the stage of first electron transfer is slowed down and the process is accompanied by chemical reactions of comproportionation (PPh_3, $\Delta E^0 = 90$ mV) and disproportionation (phosphites, $\Delta E^0 < 0$).

2.2. Kinetic regularities in reduction of organic halides under the action of Ni(0) complexes

As proved, nickel complexes in low oxidation states with π-acceptor ligands exhibit high efficiency in reactions of oxidative addition to compounds with carbon–halogen and element–halogen bonds. We have used cyclic voltammetry to investigate the kinetic regularities of this process and have followed the dynamics of the characteristic changes for reduction waves of complexes on addition of halogen-containing substrates C–Hal and E–Hal (E = element) in various solvents.

Three types of catalytic wave can be distinguished qualitatively in the voltammograms for the systems $Ni^{2+}/Ni^0,L$ (L = PPh_3, dipy) in the presence of increasing amounts of halogen-containing substrate. Firstly, a wave of catalytic reduction of the initial complex, $Ni^{2+}L_n$ (Fig. 1(a)); secondly, a wave corre-
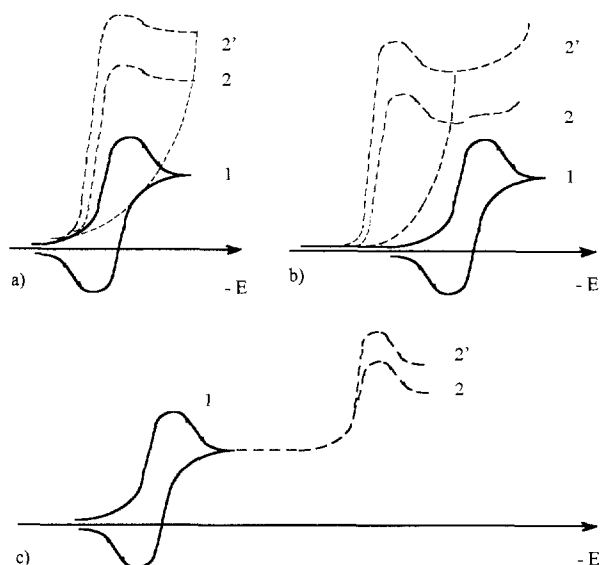
Fig. 1. Sketch of different types of voltammogram: (1) Ni(II)L$_n$ complexes; (2) Ni(II)L$_n$ complexes plus increasing amounts of organic or organoelemental halides (see text).

sponding tentatively to the reduction of a more complicated complex including the substrate as a ligand (Fig. 1(b)); thirdly, a wave of catalytic reduction of the organometallic compound, a product of the interaction between the reduced form of the initial complex and the substrate (Fig. 1(c)). The reduction voltammogram depends on the nature of the substrate, the ligand and the solvent. Probably, the following ligand–substrate–solvent systems can be assigned to the first type: dipy–Ph$_2$PCl–THF:HMPA, dipy–PhJ–THF:HMPA, dipy–Me$_3$SiCl$_3$–DMF, Ph$_3$P–Me$_3$SiCl–CH$_3$CN, Ph$_3$P–Me$_3$SiCl–THF:HMPA. Generally, the voltammogram observed may be considered as a classic one (with some differences) and the current increase can be used to calculate k_{app}, the catalyst regeneration rate constant in these systems. The systems dipy–Ph$_2$PCl–CH$_3$CN, dipy–Me$_3$SiCl–CH$_3$CN, Ph$_3$P–Ph$_2$PCl–CH$_3$CN can be assigned to be of the second type. The third type is described in considerable detail in the literature where a new more cathodic catalytic wave was attributed to the reduction of product of Ni(0) interaction with iodobenzene; this is the system Ph$_3$P–PhJ–CH$_3$CN [12–16].

The voltammetric results may be considered not only from the curve morphology viewpoint, but also from the catalytic reaction kinetics viewpoint. The nickel complex with dipy was found to be the most efficient and universal catalyst because a significant catalytic effect was observed with various substrates. In all cases a single wave with current characteristics related to the rate of the overall process of catalyst regeneration including several stages is observed. A catalytic current increase can be used to evaluate the apparent rate constant of the overall process and to divide the overall

process into separate stages by concentration relationships, with some modifications.

Let us consider the qualitative picture of the Ni^{2+} complex of dipy reduction in CH$_3$CN in more detail. The addition of substrates capable of manifesting themselves as ligands due to the availability of unshared electron pairs or vacant dπ-orbitals (P–Cl and Si–Cl) leads to the appearance of less cathodic wave with current varying in direct proportion to the substrate concentration. A linear relationship between the catalytic wave current and the substrate concentration usually shows a second-order reaction on the substrate.

Catalytic increments for phen as a ligand were observed only with organic dihalides PhPCl$_2$ and MePhSiCl$_2$ and the value of k_{app} was somewhat lower than with the dipy complex.

The voltammetric results obtained for the Ni complex with triphenylphosphine were rather complicated and could not be interpreted simply in some cases. However, they can be utilized for the qualitative and quantitative investigation of the catalysis mechanism in the most simple cases by means of literature approaches, with some allowances. If there are no additional waves in the presence of the substrate, and the complex wave grows in height with a decrease in the anodic component i_a, it is believed that the observed rate constant k_{app} calculated from the catalytic effectiveness i_k/i_d will describe the overall process including the series of successive stages where the electrochemical stage is followed by an irreversible chemical reaction.

$$P + e^- \rightleftarrows Q \quad k_s$$

$$Q + A \rightarrow [QA] \quad k_1$$

$$[QA] \rightarrow P + B \quad k_2, \text{ rapidly}$$
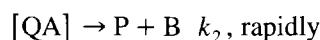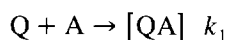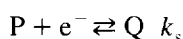
It is supposed in the case under investigation, on the basis of many literature data, that the k_1-stage of oxidative addition is the limiting one, and all other stages, including the stages of reductive elimination and successive chemical reactions, proceed rapidly. Although the scheme presented is an approximate one, various catalytic systems can be compared on this basis. As the mechanism of the catalytic reduction process of substrates with P–Cl and Si–Cl bonds is different from the classical mechanism to some degree, quantitative data on their reactivity are brought close together to a greater extent. In any case more complicated systems can be simplified under some conditions. For example, in the system

$$Ni^{2+} + nPPh_3 \rightleftarrows Ni^{2+}(Ph_3P)_n \underset{E_p}{\overset{2e^-}{\rightleftarrows}} Ni^0(Ph_3P)_n \rightleftarrows \cdots$$
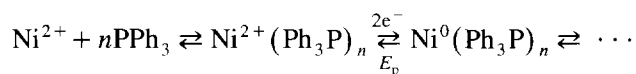
in the presence of Ph$_2$PCl(L') there is good reason to believe (based on the relative complex stability and the

equilibrium constant [17,18]) that a new wave shifted to more positive potentials which may be related to the process

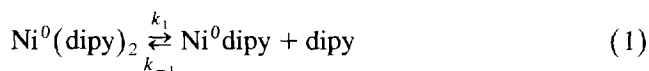$$Ni^{2+}LL' + 2e^- \underset{E_p}{\rightleftarrows} Ni^0LL'$$
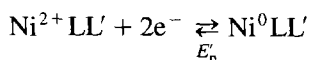
will appear in the voltammogram. It is important for quantitative evaluation that the ligand environment in the concentration range under consideration was not changed; in this case the wave at E_p should disappear and a new wave E'_p should appear instead [12].

The results show that because a wave of the initial complex does not grow in height and essentially merges

Table 1
Apparent rate constants k_{app} of substrate (RX) reduction under the action of NiL$_n$ complexes

L	Solvent	RX, $C \times 10^3$ (M)	i_k / i_d	$k_{app} \times 10^{-3}$ (M^{-1} s^{-1})
dipy	CH$_3$CN	Ph$_2$PCl		
		3.46	1.35	1.63
		5.63	2.90	4.63
		7.79	4.45	7.88
		Me$_3$SiCl		
		1.58	1.04	2.12
		3.16	2.40	5.65
		6.32	4.68	10.74
		9.49	6.72	14.75
	THF:HMPA	Ph$_2$PCl		
		9.74	5.00	7.96
		19.48	10.50	17.54
		28.58	13.00	18.32
		38.32	17.50	24.77
		Me$_3$SiCl		
		3.16	1.25	1.53
		9.49	5.13	8.58
		15.81	8.13	12.94
		28.47	14.58	18.81
		PhI		
		22.33	1.10	0.17
		45.21	1.46	0.15
		68.09	1.87	0.16
	DMF	Me$_3$SiCl		
		3.16	1.24	1.50
		9.49	1.71	0.96
		18.98	2.50	1.02
		47.45	4.55	1.35
		PhI		
		5.00	2.99	5.00
		10.00	5.29	8.60
		15.00	8.02	12.90
		20.00	11.48	19.00
PPh$_3$	CH$_3$CN	Me$_3$SiCl		
		1.58	1.60	5.02
		3.80	2.00	3.27
		9.17	4.80	7.79
		20.88	6.25	5.80
	THF:HMPA	Me$_3$SiCl		
		3.16	1.10	1.19
		9.49	1.35	0.60
		23.73	1.70	0.38
		50.93	1.85	0.21

with a wave of the new complex Ni^{2+}LL', it is possible to investigate this process on the basis of k_{app} calculation from the value i_k/i_d (Table 1). A linear dependence of k_{app} for disappearance of Ni(0) complexes on substrate R–X concentration was observed. That is, the overall process should be second order on R–X. When it is proposed that coordinatively saturated complex Ni^{0}dipy (or Ni^0(Ph$_3$P)$_2$) is a reactive particle in relation to R–X, this process may be divided into two stages, in view of the pre-equilibrium

$$Ni^0(dipy)_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Ni^0dipy + dipy \qquad (1)$$

$$Ni^0dipy + 2RX \overset{k_2}{\to} products$$

On the assumption that the equilibrium in Eq. (1) is fast and the concentration of [Ni^{0}dipy] is constant, a second-order rate constant can be obtained $k_{app} = k_1 k_2 [RX]/k_{-1}[L]$; $w = k_{app}[NiL_2][RX]$ [12].

Consequently, the rate constant of the overall reaction with the participation of the Ni(0) complex should be dependent linearly, to a first approximation, on the substrate concentration, as observed in the experiment (Fig. 2). It is seen that the angular coefficient of plots in coordinates $k_{app} - C_{RX}$ depends on solvent nature and does not depend on substrate nature. It was found that the ratio of the angular coefficients a in equations of the type $k_{app} = aC_{RX} + b$ in different solvents is equal to the reciprocal ratio of their donor numbers (L = dipy):

Solvent	Substrate	$a \times 10^6$	D_N(SbCl$_5$)[19]
CH$_3$CN	Ph$_2$PCl	1.4	14.0
	Me$_3$SiCl	1.5	
THF:HMPA	Ph$_2$PCl	0.59	29.4
	Me$_3$SiCl	0.62	
DMF	PhI	1.0	26.6

An average donor number (D_N(THF) = 20.0, D_N(HMPA) = 38.8) was determined for the mixture of the two solvents THF:HMPA (1:1).

Thus, for the solvent range:

	CH$_3$CN	DMF	THF:HMPA
a	2.4	1.7	1.0
D_N	1.0	1.9	2.4

The lower is the donor number, the steeper is the slope of the plot to the abscissa and the more efficient is the catalytic process.

2.3. The relation between electrochemical redox properties of some nickel complexes and their reactivity in coupling processes of organic and organoelemental halides

The interesting possibility of using redox potentials of organometallic compounds as starting characteristics
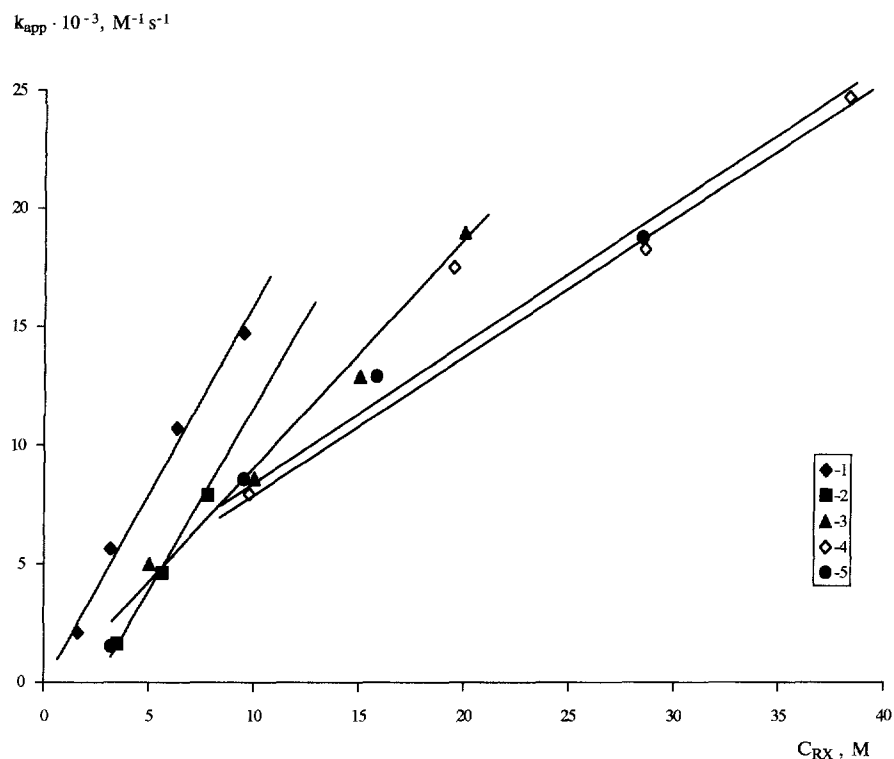
$k_{app} \cdot 10^{-3}$, $M^{-1} s^{-1}$

Fig. 2. The dependence of apparent rate constant k_{app} on substrate concentration: (1) Me_3SiCl in CH_3CN; (2) Ph_2PCl in CH_3CN; (3) PhI in DMF; (4) Ph_2PCl in THF:HMPA; (5) Me_3SiCl in THF:HMPA. The complex Ni(II) $(10^{-3}$ M) of dipy $(10^{-1}$ M) is the mediator.

for prediction of reactivity and mechanisms of reaction of organometallic compounds was found in recent years [20]. Such an approach is based on an evaluation of some redox potential functions, and well-defined physical meanings are attached to them. It is believed that such parameters as electrochemical gap G, electrochemical negativity χ, and the degree of charge transfer ΔN would be useful in investigation of reactions of various types involving a wider range of substances. Thus, the parameters G, χ and ΔN characterizing a Ni(0) com-

plex with various ligands can probably be used to evaluate the reactivity of this complex in reactions of oxidative addition to organic halides (substrates):

$$Ni^0 L_n + R-Hal \rightarrow R-Ni^{II} HalL_n$$
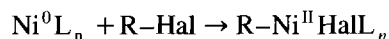
It may be suggested that the parameters characterizing the Ni(II) complex can be used to evaluate interactions between this complex and other ligands and substrates to obtain information on complexing properties, and donor–acceptor interactions between complex and
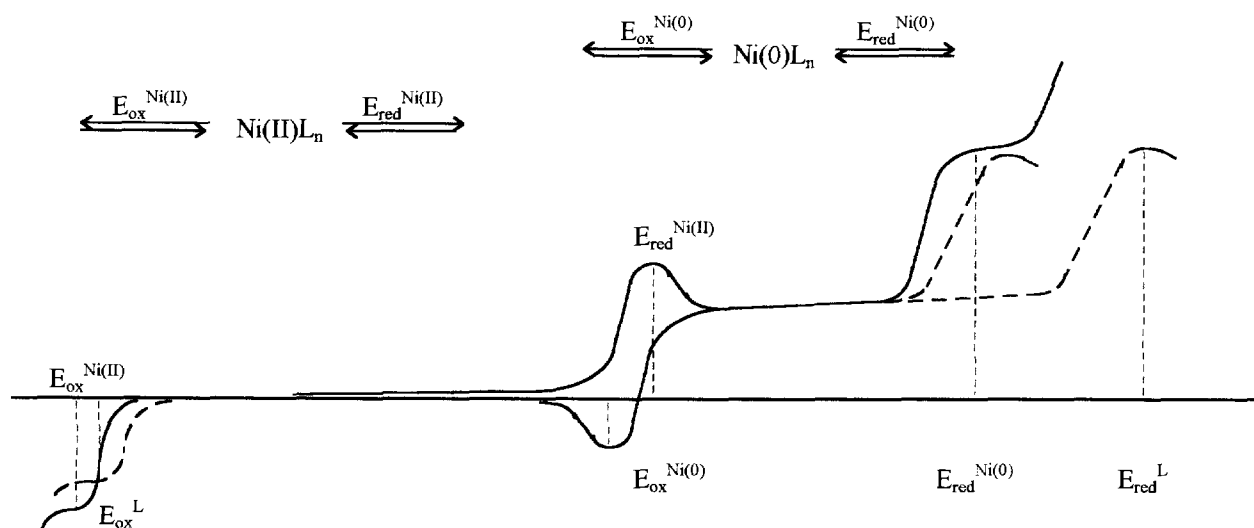

Fig. 3. Electrochemical potentials E_{ox} and E_{red} for Ni(II) and Ni(0) complexes with ligands L.

substrate. This is especially of current interest in relation to organophosphorus substrates capable of exhibiting σ-donor and π-acceptor properties in interactions with transition metals.

The procedure of E_{ox} and E_{red} measurements for Ni(II) and Ni(0) complexes has been described fully previously [9]. For every Ni(II) and Ni(0) complexes there are inherent values of oxidation and reduction potentials and electrochemical gaps (Fig. 3):

$$G(Ni(0)L_n) = E_{ox}^{Ni(0)} - E_{red}^{Ni(0)} G(Ni(II)L_m)$$

$$= E_{ox}^{Ni(II)} - E_{red}^{Ni(II)}$$

In order to solve the tasks to be sought, we experimentally evaluate the necessary values of potentials and electrochemical gaps $G = E_{ox} - E_{red}$ and electrochemical negativity $\chi = (E_{ox} + E_{red})/2$ for the range of Ni(II) and Ni(0) complexes under investigation [9] (Table 2). The complex of Ni(II) with dipy has the largest value of electrochemical gap, characterized as the degree of 'rigidity'. This value is appreciably less for phosphine and phosphite complexes of Ni(II). The opposite dependence is observed in the case of Ni(0) complexes, i.e. the least value of electrochemical gap G, and therefore the greatest donor ability and polarizability, are characteristic of Ni(0) complexes with dipy (0.60 V); next are Ni(0) complexes with phen (0.72 V) and with PPh$_3$ (1.04 V).

The values of charge transfer degree between the two complexes and substrates $\Delta N = \Delta\chi/\Sigma G = (\chi_a - \chi_d)/(G_a + G_d)_d$ were calculated on the basis of G and

Table 2
Redox potentials, and electrochemical functions G and χ for the complexes of Ni(II) and Ni(0) and substrates

Ligands, substrates	$-E_{red}$ (V)	E_{ox} (V)	G	$-\chi$
Ni(II) or [Ni(0)] complex				
dipy	1.68	1.66	3.34	0.01
	[2.20]	[−1.60]	[0.60]	[1.90]
Ph$_3$P	1.11	0.96	2.07	0.08
	[2.05]	[−1.01]	[1.04]	[1.53]
(PhO)$_3$P	1.35	1.10	2.45	0.12
	[2.89]	[−0.95]	[1.85]	[1.92]
PhP(OBu)$_2$	0.89	1.12	2.01	−0.12
	[2.20]	[−0.55]	[1.65]	[1.38]
(^{i}PrO)$_3$P	1.14	1.12	2.26	0.01
	[3.18]	[−0.62]	[2.56]	[1.90]
(Me$_2$N)$_3$P	1.80	0.80	2.60	0.50
	[3.47]	[−1.50]	[1.97]	[2.49]
phen	0.84	1.37	2.21	0.27
	[1.54]	[−0.82]	[0.72]	[1.18]
Substrates				
PhBr	2.83	2.18	5.01	0.33
Ph$_2$PCl	2.27	1.50	3.77	0.39
PhPCl$_2$	1.10	1.67	2.77	−0.29
PCl$_3$	1.26	1.74	3.00	−0.24
C$_6$H$_{13}$I	2.30	1.90	4.20	0.20
CH$_2$Br$_2$	2.72	1.89	4.61	0.42

Table 3
Charge transfer degree between the complexes of Ni(II) and Ni(0) (given in brackets) and the substrates PhBr, Ph$_2$PCl PhPCl$_2$ and PCl$_3$

Ligand	$\Delta N \times 10^2$			
	PhBr	Ph$_2$PCl	PhPCl$_2$	PCl$_3$
dipy	−4 [28]	−5 [37]	5 [71]	4 [60]
Ph$_3$P	−4 [20]	−5 [27]	7 [55]	6 [44]
phen	−1 [15]	−3 [18]	0 [42]	—
(PhO)$_3$P	−3 [23]	−4 [33]	8 [60]	7 [45]
PhP(OBu)$_2$	−6 [16]	−8 [22]	4 [46]	3 [35]
(^{i}PrO)$_3$P	−4 [21]	−7 [30]	6 [54]	5 [38]
(Me$_2$N)$_3$P	2 [31]	2 [44]	1 [74]	1 [55]

χ assuming that the Ni (II or 0) complex is a donor (d) and the substrate is an acceptor (a) of electrons (Table 3). The results show that bromobenzene has a very large electrochemical gap, i.e. its molecule is hard to polarize and has weak electron donor properties. In this case, the degree of charge transfer for Ni(II) complexes with substrates is small and for Ni(0) complexes is one order of magnitude greater, thus pointing to the occurrence of oxidative addition in the latter case. The sign of the charge transfer degree shows that the Ni(0) complex manifests pronounced donor properties with all substrates ($\Delta N \gg 0$). Phosphorus chlorides, PCl$_3$ and PhPCl$_2$, exhibit acceptor properties in relation to all Ni(II) complexes, and Ph$_2$PCl has more distinct donor properties. One can use the foregoing data of voltammetric measurements, quantum-chemical calculations and evaluated values of G, χ and ΔN to explain the observed reactivity of nickel complexes in catalytic processes. The catalytic current increase on voltammograms of complexes on addition of substrates was observed only in the case of nickel complexes with dipy, phen and PPh$_3$. That is, catalyst regeneration in this case is sufficiently fast on the time scale of the method used. However, complex Ni^0(phen) has a lesser ΔN value than the dipy and PPh$_3$ complexes and, therefore, the rate constant must be less, as is observed in the experiment. Probably, this could be due to the large difference of reduction potentials E^0, and, therefore, standard potentials E of complex and substrate $\Delta E^0 = E_{HOMO}^{complex} - E_{LUMO}^{substrate}$: (LUMO is the lowest unoccupied molecular orbital; HOMO is the highest occupied molecular orbital).

On addition of Ph$_2$PCl to the solution of Ni(II) complex with dipy or PPh$_2$ a catalytic wave at less negative potentials than E_p of the initial complex was observed. In the case of PhPCl$_2$ and PCl$_3$, E_p values of complexes are more negative than the corresponding values of the substrates, and the waves of phosphorus chlorides in the presence of substrate excess are superimposed on the complex wave.

When considering the redox properties of complexes, account must be taken of some factors related to the

electron transfer kinetics and subsequent chemical reactions. As both initial compounds and reduction products are nickel complexes in different oxidation states, and the overall reduction process is close to reversible or quasi-reversible, the direction and shift value of the wave is bound to depend on the relative stability of the components of this redox pair, the difference between their coordination numbers and the equilibrium constant. Quantum-chemical calculations of the electron structure of Ni(0) complexes with organophosphorus ligands show that the Ni-P bond is more stable if a halogen rather than a phenyl group is the substituent at the phosphorus atom; this is explained by the greater additive π-binding between the filled σ-orbital of the metal and the loose orbital of phosphorus (which is a combination of 3d and 3p orbitals with the 3p orbital predominating) and a greater population of the molecular orbital in the ligand complex. Steric factors are of little influence on the stability of the metal-ligand bond because the van der Waals [21] radii of Ph and Cl are close together (1.7 Å and 1.8 Å respectively); thus, changing Ph to Cl will not elongate the Ni-P bond as, for example, in the case of the bulky butyl substituent.

The low oxidation state of the metal and the strong electronegative substituents in the phosphine ligand are favourable for π-binding. The anodic shift of the nickel(II) wave on addition of PPh_3 described previously [22] suggests that a reduced form of metal gives a more stable complex than its oxidized form. In addition, a second factor, the removal of the overvoltage for nickel ion reduction on phosphine addition is in operation. Ph_3PCl as a ligand behaved in a similar manner, though the shift $\Delta E_p / \Delta \log C_L$ on its addition to a solution of the nickel salt was much greater (about 40 mV for PPh_3 and 65 mV for $PhPCl_2$). Thus, the following conclusion can be drawn: Ph_2PCl gives a more stable complex with the reduced nickel form than Ph_3P, and complexes of Ph_3P and Ph_2PCl are more stable with Ni(0) than with Ni(II). The question of bond stability of these ligands with Ni(II) remains open. In this case, π-donation is not a determining and characteristic factor. The stability of the complex will depend on the σ-donor ability of ligand. It is assumed that the σ-donor ability depends on the basicity, and more basic ligands form more stable bonds. The basicity of Ph_3P is somewhat lower than the basicity of Ph_2PCl, and, as a consequence, the complex $Ni^{2+}-Ph_3P$ will be slightly more stable (in the context of a hard-soft acid-base principle this is an interaction of a medium power acid Ni(II) with a soft base Ph_3P).

Thus, a wave appearing at less negative potentials on addition of Ph_2PCl to the solution of $Ni^{2+}-Ph_3P$ can be explained by Ph_2PCl complexation and the ratio of the complex stability constants to components of the system Ni^{2+}/Ni^0.

It is just complex Ph_2PCl with nickel in various oxidation states (II and 0) which takes part in the catalytic cycle.

The behaviour of the system $Ni^{2+}/Ni-dipy$ in the presence of Ph_2PCl is of a complicated character. Though data on competitive ability to complexation with nickel in various oxidation states for these ligands are absent in the literature, some analogies may be given. According to ligand field theory, both dipyridyl and Ph_3P are ligands with great field force splitting levels [23]. Calculated degrees of charge transfer between these complexes and Ph_2PCl (Table 3) are close to each other. Unoccupied π-orbitals are favourable for π-binding and transfer of d-electrons from metal to ligand. However, π-donation in this case is possible with the Ni^{2+} ion too; nevertheless, σ-donor bonds are dominant. Probably, the Ni-dipy complex is more stable than the Ni(0)-dipy complex because ligand addition shifts the nickel wave to a more cathodic region [12]. A larger wave shift in the Ni(II) reduction to less cathodic potentials on addition of Ph_2PCl is also explained by the formation of a more stable Ph_2PCl complex with Ni(0) than with Ni(II).

It is believed that the highest reactivity of Ni(0) complexes with dipy and Ph_3P (compared with the other complexes investigated) in coupling reactions (with large k_{app}) is related, in a way, to the small value of the electrochemical gap G. The smaller is the G value, the greater are the donor properties and polarizability of the complex. This is, probably, the deciding factor in this case.

Catalytic properties of complexes with organophosphorus ligands can be determined generally by the electron and steric effects of these ligands. The complex with Ph_3P having the lowest value of the electron parameter and the maximum cone angle θ characterizing the large steric effect is the most efficient catalyst among the complexes investigated. The steric effect determines the equilibrium of the complex dissociation

$$Ni^0L_4 \overset{K_d}{\rightleftharpoons} Ni^0L_2 + 2L$$
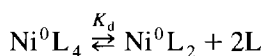
As the coordinatively unsaturated complex Ni^0L_2 operates as a direct catalyst in dehalogenation reactions, spatially loaded ligands will determine a large part of the value of the dissociation constant K_d. The same is true for dissociation rates: phosphines dissociate faster from Ni(0) complexes than similar-sized phosphites. Probably, an equilibrium of ligand exchange, for example Ph_3P for Ph_2PCl (substrate and ligand), must play some part in reactions of oxidative addition to the Ni(0) complex. The greater is this equilibrium shifted to the substrate side, then the easier the reaction runs. In this respect, phosphites bonding more rigidly with Ni(0) adversely affect the catalytic properties of the latter.

Redox reactions of disproportionation and comproportionation are likely to be characteristic for Ni(II)

complexes having greater polarizability, and softness due to small values of the electrochemical gap (phosphines and phosphites). The performance of competitive reactions must have an adverse effect on the catalytic efficiency of these complexes in dehalogenation reactions, since the concentration of the active catalyst form in the reaction zone diminishes, and the faster the reaction the higher is the rate of these redox reactions. In addition, the results of preparative reductive electrolysis of $Ni[(PhO)_3P]_4^{2+}$ revealed that, in this case, the reaction of electron transfer with rupture of the P–OPh bond in the inner sphere of the complex and formation of phenylphosphonite took place.

The catalytic efficiency in a series of phosphine and phosphite complexes with nickel will be determined by the rate ratio of the separate stages in the overall process-target reactions leading to formation of the terminal desired product, and competitive processes. The complex with dipy, in the reduction of which competitive redox reactions are absent, has the best catalytic efficiency. This factor is also favourable for the sufficiently high catalytic efficiency of the complex with phen. However, the reaction rate must be lower due to the lower value (compared with Ph_3P and dipy complexes) of the degree of charge transfer ΔN (which is as observed). Thus, the following factors are of importance in evaluation of the catalytic activity of the Ni(0) complex in reactions of oxidative addition: the value of the electrochemical gap G, the degree of charge transfer ΔN, the stability of the Ni–P bond, electronic and steric effects of the ligands, the availability or absence of homogeneous redox reactions; consideration of only one of these individual factors prevents one from drawing the correct conclusions.

3. Experimental section

3.1. Apparatus

Cyclic voltammograms were registered at a glassy carbon electrode with 1.5 mm diameter in a thermostatically controlled cell in an argon atmosphere. A silver electrode $Ag/AgNO_3$ (0.01 M solution in CH_3CN) served as a reference electrode. Curve registration was made using a PI-50-1 (USSR) potentiostat.

3.2. Voltammetric measurements

In order to obtain the kinetic characteristics of the process, the voltammograms were recorded for each

system consisted of the substrate and the nickel complex. The concentration of $Ni(BF_4)_2$, first dried in a vacuum at 40 °C over 2 days, was 5×10^{-3} M, and the concentration of ligands was $(1.5–2.0) \times 10^{-2}$ M. All substrates were freshly distilled in vacuum and were added to the electrochemical cell which was deoxygenated by argon bubbling. The calculation of the rate constant of catalyst regeneration k_{app} was performed by the method in Ref. [24].

References

[1] G. Bontempelli, S. Daniele and M. Fiorani, Ann. Chim. (Rome), 75 (1985) 19.
[2] G. Bontempelli and M. Fiorani, Ann. Chim. (Rome), 75 (1985) 303.
[3] C. Amatore and A. Jutand, Acta Chem. Scand., 44 (1990) 755.
[4] H. Marzouk, Y. Rollin, J. Folest, J.Y. Nedelec and J. Perichon, J. Organomet. Chem., 369 (1989) 47.
[5] C. Amatore and A. Jutand, Organometallics, 7 (1988) 2203.
[6] A. Conan, S. Sibille, E. d'Incar and J. Perichon, J. Chem. Soc. Chem. Commun., (1980) 48.
[7] Yu.M. Kargin, V.V. Zhuikov, Yu.H. Budnikova and D.S. Fattakhova, Electrochemistry (Russ.), 28 (1992) 615.
[8] Yu.H. Budnikova and Yu.M. Kargin, J. Gen. Chem. (Russ.), 63 (1993) 1038.
[9] Yu.H. Budnikova and Yu.M. Kargin, J. Gen. Chem. (Russ.), 65 (1995) 1536.
[10] S. Daniele, G. Bontempelli, F. Magno and M. Fiorani, Ann. Chim. (Rome), 78 (1988) 363.
[11] Yu.H. Budnikova, O.E. Petrukhina, N.N. Gudina and Yu.M. Kargin, J. Gen. Chem. (Russ.), 66 (1996) 610.
[12] Yu.H. Budnikova, A.M. Yusupov and Yu.M. Kargin, J. Gen. Chem. (Russ.), 64 (1994) 1153.
[13] G. Shiavon, G. Bontempelli, M. De Nobili and B. Corain, Inorg. Chim. Acta, 42 (1980) 149.
[14] G. Shiavon, G. Bontempelli, F. Magno and S. Daniele, J. Electroanal. Chem., 140 (1982) 91.
[15] G. Bontempelli, S. Daniele and M. Fiorani, J. Electroanal. Chem., 160 (1984) 249.
[16] G. Shiavon, G. Bontempelli and B. Corain, J. Chem. Soc. Dalton Trans., (1981) 1074.
[17] E. Vincent, L. Verdonek and G.P. Van Der Kelen, J. Mol. Struct., 65 (1980) 239.
[18] M. Braga, J. Mol. Struct. (Theochem), 253 (1992) 167.
[19] J.E. Gordon, The Organic Chemistry of Electrolyte Solutions, Wiley, New York, 1975.
[20] K.P. Butin, V.V. Strelets and O.A. Reutov, Metalloorg. Chim. (Russ.), 3 (1990) 814.
[21] C. Wilkinson, F.G.A. Stone and E.W. Abel, Comprehensive Organometallic Chemistry, Vol. 6, Wiley, Oxford, 1992.
[22] Yu.H. Budnikova and Yu.M. Kargin, J. Gen. Chem. (Russ.), 65 (1995) 1655.
[23] L.A. Nikolaev, Inorganic Chemistry, Prosveshchenie, Moscow, 1992.
[24] C.P. Andrieux and J.-M. Saveant, Electrochemical reactions, in C.F. Bernascon (ed.), Investigations of Rates and Mechanisms, Vol. 6, 41 E, Part 2, Wiley, New York, 1986, p. 305.