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New method of metal-induced oxidative phosphorylation of benzene*

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A new approach to phosphorylation of benzene with diethyl phosphite is suggested, which is based on the electrocatalytic oxidation of a mixture of benzene and diethyl phosphite (1 : 1) under mild conditions (room temperature, normal pressure) in the presence of bimetallic catalytic systems $Mn^{II}/Co^{II}L$ ($MnSO_4/CoCl_2$dmphen or $MnCl_2/CoCl_2$bipy). This method gives diethyl phenylphosphonate in high yield (up to 90%) and practically 100% conversion of the phosphite.

Key words: phosphorylation, oxidation, electrosynthesis, catalyst, metal, complex, C—H functionalization.

Dialkyl arylphosphonates are important intermediates in the synthesis of pesticides and biologically active compounds.[1—4] There are several traditional methods for the synthesis of dialkyl arylphosphonates. Among them, phosphorylation of aryl halides[5—13] is the most frequently used reaction. There are known separate examples of radical phosphorylation of aromatic compounds with diethyl phosphite, for example, naphthalene in the presence of *tert*-butyl peroxide,[14] a number of arenes in the presence of oxidants $(NH_4)_2[Ce(NO_3)_6]$ (see Ref. 15) or $Na_2S_2O_8$ and $AgNO_3$,[16] $Mn^{II}/Co^{II}/O_2$.[17] The most successful phosphorylation of benzene with Ishii dialkyl phosphite[17] has a number of disadvantages: an elevated temperature of the reaction and not very high conversion of the substrates to the monophosphorylation product, which in the case of benzene is 6% (25 °C) and 69% (60 °C). Arylphosphonates were obtained[18,19] in up to 59% yield by electrochemical oxidation of trialkyl phosphites in the presence of benzene or its derivatives at the 5 : 1 ratio of benzene : diethyl phosphite in acetonitrile in the presence of a supporting salt $NaClO_4$. An electrochemical oxidative phosphorylation was suggested[20] for benzene nitro derivatives with phosphorus(III) compounds, including diethyl phosphite. However, this approach cannot be used for unsubstituted benzene, since a key step of the process is a nucleophilic addition of H-phosphonate to the aromatic ring (S_NAr-mechanism), followed by the oxidation of the σ-H-adducts. A method for phosphorylation of benzene derivatives was also elaborated.[21]

The synthesis of arylphosphonates by a direct phosphorylation of a C—H bond in aromatic substrates remains one of the most important approaches, since it meets the generally accepted criteria of "green chemistry". In this connection, a search for the catalytic conditions is especially promising, since there are only few catalytic phosphorylation reactions of aromatic compounds. Perhaps, benzene in this regard is one of the most problematic objects, since its structure lacks factors facilitating a C—H substitution, *i.e.*, functional group which activate bonds or direct functionalization. As a rule, if conditions for phosphorylation of benzene are selected properly, its derivatives give even higher yields of the target products.[17—19]

Phosphorylation of benzene by the methods described above does not give high product yields or conversion. We suggested that phosphorylation of benzene at room temperature in one step would be feasible using advantages of electrochemical metal complex catalysis.[22,23] As the catalytic systems for electrochemical phosphorylation of benzene, we have chosen metal complexes and salts (M) in the oxidation state II, which can undergo electrochemical oxidation to M^{III}: $PdCl_2$bipy (bipy stands for 2,2´-bipyridyl), manganese citrate $Mn_3(C_6H_5O_7)_2$, $Mn_3(C_6H_5O_7)_2/CoCl_2$dmphen (dmphen stands for 1,10-dimethylphenanthroline), $MnCl_2$, $MnCl_2/CoCl_2$dmphen, $MnCl_2/CoCl_2$bipy, $MnSO_4$, $MnSO_4/Ni(BF_4)_2$bipy, $MnCl_2$bipy, $Ni(BF_4)_2$dmphen, and $CoCl_2$dmphen. The process was conducted with the equimolar benzene : dialkyl phosphite ratio (1 : 1) at room temperature, which earlier have never given good yields of arylphosphonate (Scheme 1, Table 1). The catalytic systems were tested using commercially available, relatively stable and inexpensive phosphorylting agent — diethyl phosphite.

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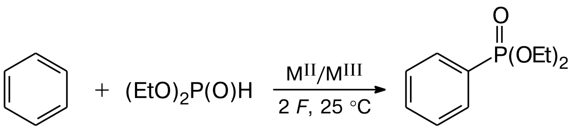
Table 1. Electrochemical phosphorylation of benzene with diethyl phosphite (taken in the ratio 1 : 1) in the presence of various catalysts[a]

Catalytic system	Content of catalyst (mol.%)	MeCN : AcOH[b]	Yield of $PhP(O)(OEt)_2$ (%)
$PdCl_2$bipy	10	1 : 0	—
$Mn_3(C_6H_5O_7)_2$	10	1 : 2	10
		1 : 1	22
		2 : 1	10
$Mn_3(C_6H_5O_7)_2/CoCl_2$dmphen	10/0.5	1 : 2	—
		1 : 1	15
		2 : 1	25
$MnCl_2$	1	1 : 2	—
		1 : 1	—
		2 : 1	30
$MnCl_2/CoCl_2$dmphen	10/0.5	1 : 2	10
		1 : 1	50
		2 : 1	90
$MnCl_2/CoCl_2$bipy	10/0.5	2 : 1	90
$MnSO_4$	1	1 : 2	—
		1 : 1	—
		2 : 1	Traces
$MnSO_4/CoCl_2$dmphen	10/0.5	2 : 1	90
$MnSO_4/Ni(BF_4)_2$bipy	10/10	2 : 1	30
$MnCl_2$bipy	10	1 : 0	35
$Ni(BF_4)_2$dmphen	10	1 : 0	5
$CoCl_2$dmphen	0.5	1 : 0	15
$MnCl_2/CoCl_2$	10/1		10
—		1 : 0	5

[a] Conditions: ~20 °C, $Q = 2\ F$ per 1 mole of diethyl phosphite, galvanostatic mode.

[b] Acetic acid was added to increase the solubility of manganese salts.

Scheme 1



The concentration of each component of the catalytic systems was determined with allowance for its solubility and activity (manganese compounds are poorly soluble under these conditions, therefore, they were used in the maximum attainable concentration).

As it follows from Table 1, the most efficient catalytic systems are $MnSO_4/CoCl_2$dmphen and $MnCl_2/CoCl_2$bipy. The phosphorylation virtually does not occur in the absence of the catalysts. It is important to point out that in these syntheses a 100% conversion of diethyl phosphite is reached after passing 2 *F* of electricity. In contrast to the results published earlier[17] (according to which no phosphorylation takes place at all in the absence of $Mn(OAc)_2$), under our conditions the phosphonate can be also obtained in the presence of a mono-component catalyst (both Mn^{II} and Co^{II}), though in this case the yield of the target product is considerably lower. It should be noted that the earlier undescribed pair Mn^{II}/Mn^{III} does catalyze the phosphorylation of benzene under oxidative conditions, though with not very high yield of diethyl phenylphosphonate (30%, see Table 1). Apart from that, a difficult to separate mixture of phosphorylation products (mono, di, tri) is obtained in this case.

To find out the factors influencing efficiency of electrocatalytic phosphorylation, we used a CVA method to determined electrochemical parameters for all the catalyst complexes (Table 2).

It should be noted that diethyl phosphite and benzene under the selected conditions do not form oxidation peaks on the CVA curves. However, their addition to the solutions of catalyst complexes leads to considerable changes in the CVA curves. For example, the unsaturated complex $CoCl_2$bipy undergoes a one-electron oxidation at the peak potential of 1.34 V, whereas after the addition of $HP(O)(OEt)_2$ to its solution (Fig. 1), the CVA curve exhibits a new quasi-reversible anode peak at a 0.54 V potential. The further addition of the increasing amounts of $HP(O)(OEt)_2$ (1 : 1, 1 : 2, 1 : 3, 1 : 6, 1 : 9, 1 : 27) (see Fig. 1) influences the voltamperogram little. It can be suggested that the cobalt complex reacts with diethyl phosphite to form a new complex, which oxidizes at lower potentials.

Table 2. The values of potentials (E_P) and currents (i) for the first peaks of oxidation of complexes and salts (C = 0.5 mmol L^{-1}) used for phosphorylation of benzene[a]

Complex/metal salt	E_p/V	i/μA
$NiBF_4$dmphen	0.90	68
$CoCl_2$dmphen	1.51	35
$CoCl_2$bipy	1.34	35
$MnCl_2$bipy	1.14	32
$MnCl_2$	1.27	70
$MnSO_4$[b]	1.34	19

[a] Conditions: working electrode glassy carbon, reference electrode Ag/AgCl, ~20 °C, supporting salt Bu_4NBF_4, MeCN.

[b] Paste electrode: carbon (0.0009 g)/$Bu^t_3PC_{12}H_{25}BF_4$ (0.0005 g)/$MnSO_4$ (0.0007 g).

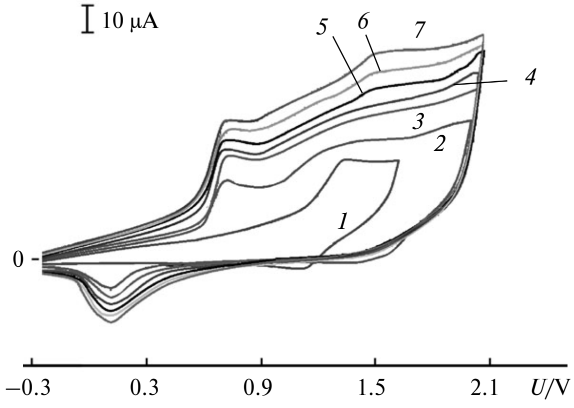


Fig. 2. CVA curves of complex $CoCl_2$bipy ($5 \cdot 10^{-4}$ mol L^{-1}) in the presence of increasing amounts of $HP(O)(OEt)_2$ and benzene with the ratio $CoCl_2$bipy : $HP(O)(OEt)_2$: C_6H_6 = 1 : 0 : 0 (*1*), 1 : 1 : 1 (*2*), 1 : 2 : 2 (*3*), 1 : 3 : 3 (*4*), 1 : 4 : 4 (*5*), 1 : 5 : 5 (*6*), and 1 : 6 : 6 (*7*) in MeCN; Et_4NBF_4, reference electrode Ag/AgCl.

Upon addition of benzene to a solution of $CoCl_2$bipy containing $HP(O)(OEt)_2$ (Fig. 2), the anode quasi-reversible peak is slightly shifted, and the oxidation occurs at a 0.70 V potential. It should be noted that the addition of a mixture of substrates ($HP(O)(OEt)_2$ and benzene) to the catalyst $CoCl_2$bipy leads to a catalytic increase in current (see Fig. 2). Thus, the complex : phosphite : benzene ratio equal to 1 : 6 : 6 gives i_{cat}/i_{dif} = 2.

Similar changes in the CVA curves are observed in the case of the catalyst $CoCl_2$dmphen in the presence of the substrates. In turn, the CVA curves of $CoCl_2$bipy and $CoCl_2$dmphen upon addition of increasing amounts of benzene (in the absence of phosphite) remain unchanged.

In the case of $Ni(BF_4)_2$dmphen, the changes in the CVA curves in the presence of $HP(O)(OEt)_2$ are also similar to those observed for $CoCl_2$bipy (see Fig. 1), in particular, emerges a new quasi-reversible anode peak (E_p = 0.5 V), which changes little as the content of $HP(O)(OEt)_2$ in the solution increases (Fig. 3).

The oxidation of the system $Ni(BF_4)_2$dmphen in the presence of $HP(O)(OEt)_2$ and benzene (Fig. 4) occurs at slightly more positive potential (E_p = 0.75 V), the oxidation peak has a complicated shape. Under identical conditions, a higher catalytic current efffect is observed as compared to cobalt catalysts: the i_{cat}/i_{dif} value reaches 4.1 at the ratio [$Ni(BF_4)_2$dmphen] : [$HP(O)(OEt)_2$] : C_6H_6 = = 1 : 6 : 6.

The oxidation voltamperogram of complex $MnCl_2$bipy in the presence of increasing amounts of $HP(O)(OEt)_2$ (Fig. 5) somewhat differs from those for $CoCl_2$bipy and $Ni(BF_4)_2$dmphen described above. A one-electron oxida-

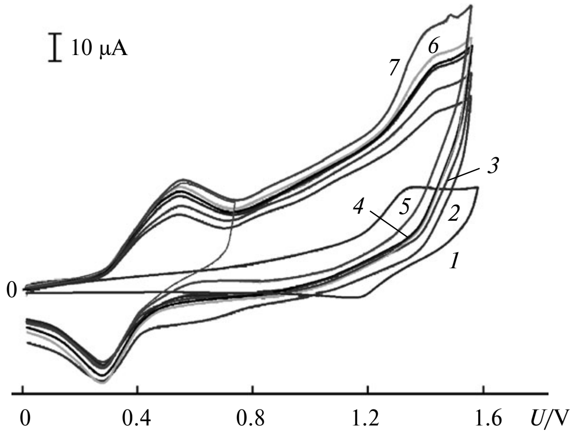


Fig. 1. CVA curves of complex $CoCl_2$bipy ($5 \cdot 10^{-4}$ mol L^{-1}) in the presence of increasing amounts of $HP(O)(OEt)_2$ with the ratio $CoCl_2$bipy : $HP(O)(OEt)_2$ = 1 : 0 (*1*), 1 : 1 (*2*), 1 : 2 (*3*), 1 : 3 (*4*), 1 : 6 (*5*), 1 : 9 (*6*), and 1 : 27 (*7*) in MeCN; Et_4NBF_4, reference electrode Ag/AgCl.

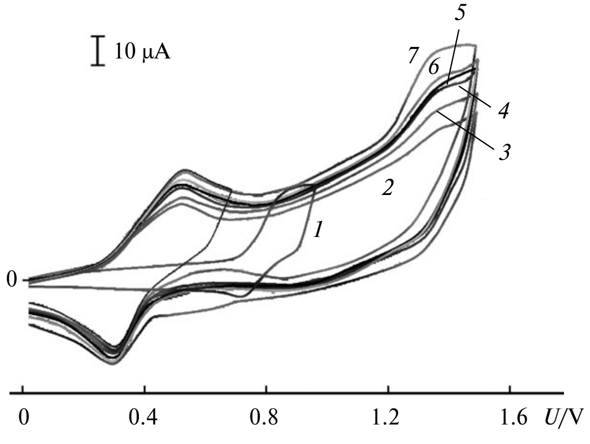


Fig. 3. CVA curves of complex $Ni(BF_4)_2$dmphen ($5 \cdot 10^{-4}$ mol L^{-1}) in the presence of increasing amounts of $HP(O)(OEt)_2$ with the ratio $Ni(BF_4)_2$dmphen : $HP(O)(OEt)_2$ = 1 : 0 (*1*), 1 : 1 (*2*), 1 : 2 (*3*), 1 : 3 (*4*), 1 : 6 (*5*), 1 : 9 (*6*), and 1 : 27 (*7*) in MeCN; Et_4NBF_4, reference electrode Ag/AgCl.

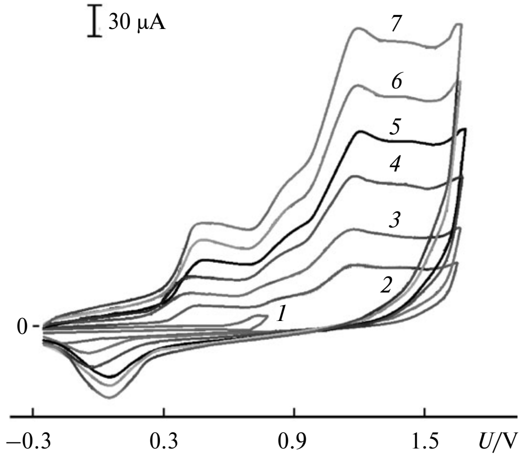


Fig. 4. CVA curves of complex $Ni(BF_4)_2$dmphen ($5 \cdot 10^{-4}$ mol L^{-1}) in the presence of increasing amounts of $HP(O)(OEt)_2$ and benzene with the ratio $Ni(BF_4)_2$dmphen : $HP(O)(OEt)_2$: C_6H_6 = = 1 : 0 : 0 (*1*), 1 : 1 : 1 (*2*), 1 : 2 : 2 (*3*), 1 : 3 : 3 (*4*), 1 : 4 : 4 (*5*), 1 : 5 : 5 (*6*), and 1 : 6 : 6 (*7*) in MeCN; Et_4NBF_4, reference electrode Ag/AgCl.

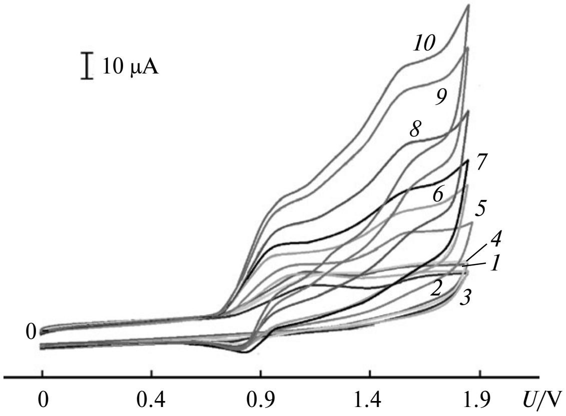


Fig. 5. CVA curves of complex $MnCl_2$bipy ($5 \cdot 10^{-4}$ mol L^{-1}) in the presence of increasing amounts of $HP(O)(OEt)_2$ with the ratio $MnCl_2$bipy : $HP(O)(OEt)_2$ = 1 : 0 (*1*), 1 : 1, 1 : 2, 1 : 3 (*2*), 1 : 6 (*3*), 1 : 24 (*4*), 1 : 48 (*5*), 1 : 72 (*6*), 1 : 96 (*7*), 1 : 120 (*8*), 1 : 144 (*9*), and 1 : 168 (*10*) in MeCN; Et_4NBF_4, reference electrode Ag/AgCl.

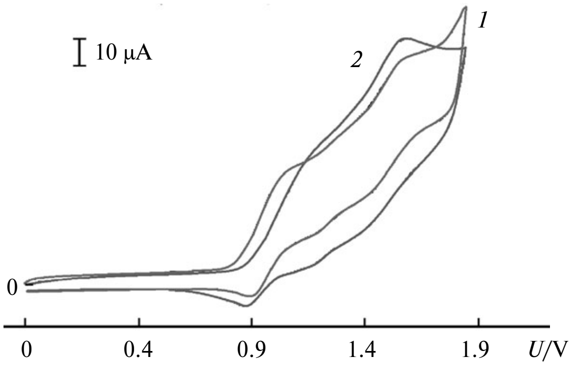


Fig. 6. CVA curves of complex $MnCl_2$bipy ($5 \cdot 10^{-4}$ mol L^{-1}) in the presence of $HP(O)(OEt)_2$ (1 : 168) (*1*), as well as $MnCl_2$bipy in the presence of $HP(O)(OEt)_2$ and benzene (1 : 168 : 168) (*2*) in MeCN; Et_4NBF_4, reference electrode Ag/AgCl.

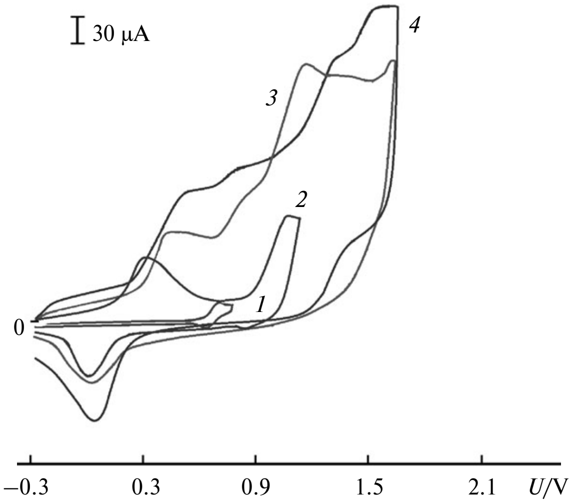


Fig. 7. CVA curves of complex $Ni(BF_4)_2$dmphen ($5 \cdot 10^{-4}$ mol L^{-1}) (*1*), $Ni(BF_4)_2$dmphen in the presence of $HP(O)(OEt)_2$ (1 : 6) (*2*), $Ni(BF_4)_2$dmphen in the presence of $HP(O)(OEt)_2$ and benzene (1 : 6 : 6) (*3*), as well as $Ni(BF_4)_2$dmphen in the presence of $MnCl_2$bipy, $HP(O)(OEt)_2$ and benzene (1 : 1 : 6 : 6) (*4*) in MeCN; Et_4NBF_4, reference electrode Ag/AgCl.

Table 3. The increase in current of the first peaks of oxidation of catalytic systems used for phosphorylation of benzene at ~20 °C

System	Ratio	i_{cat}/i_{dif}
$CoCl_2$bipy—$HP(O)(OEt)_2$—C_6H_6	1 : 6 : 6	2.07
$CoCl_2$dmphen—$HP(O)(OEt)_2$—C_6H_6	1 : 6 : 6	2.97
$MnCl_2$bipy—$HP(O)(OEt)_2$—C_6H_6	1 : 6 : 6	2.13
$Ni(BF_4)_2$dmphen—$HP(O)(OEt)_2$—C_6H_6	1 : 6 : 6	4.10
$CoCl_2$dmphen—$MnCl_2$bipy—$HP(O)(OEt)_2$—C_6H_6	0.05 : 1 : 6 : 6	3.17
$CoCl_2$bipy—$MnCl_2$bipy—$HP(O)(OEt)_2$—C_6H_6	0.05 : 1 : 6 : 6	2.73
$Ni(BF_4)_2$dmphen—$MnCl_2$bipy—$HP(O)(OEt)_2$—C_6H_6	0.05 : 1 : 6 : 6	6.13

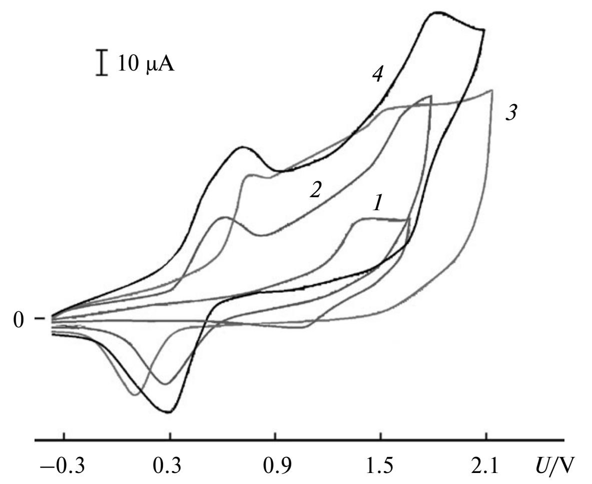
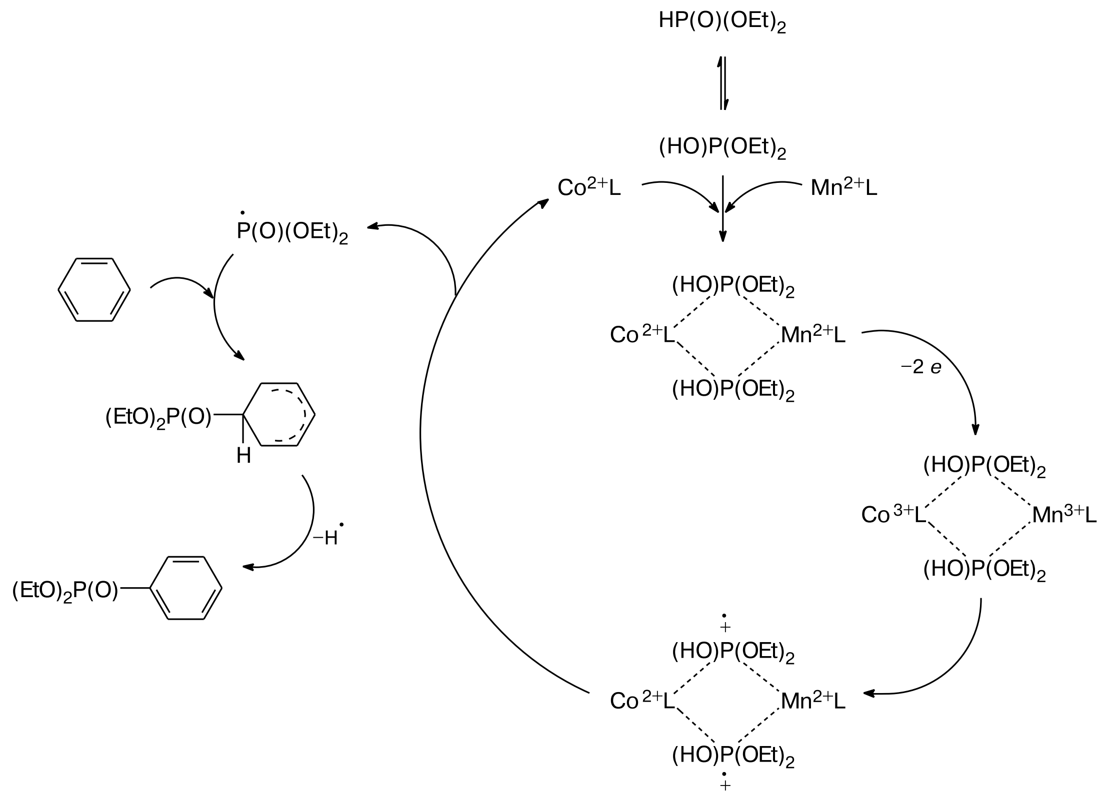


Fig. 8. CVA curves of complex $CoCl_2$bipy ($5 \cdot 10^{-4}$ mol L^{-1}) (*1*), $CoCl_2$bipy in the presence of $HP(O)(OEt)_2$ (1 : 6) (*2*), $CoCl_2$bipy in the presence of $HP(O)(OEt)_2$ and benzene (1 : 6 : 6) (*3*), as well as $CoCl_2$bipy in the presence of $MnCl_2$bipy, $HP(O)(OEt)_2$ and benzene (1 : 1 : 6 : 6) (*4*) in MeCN; Et_4NBF_4, reference electrode Ag/AgCl.

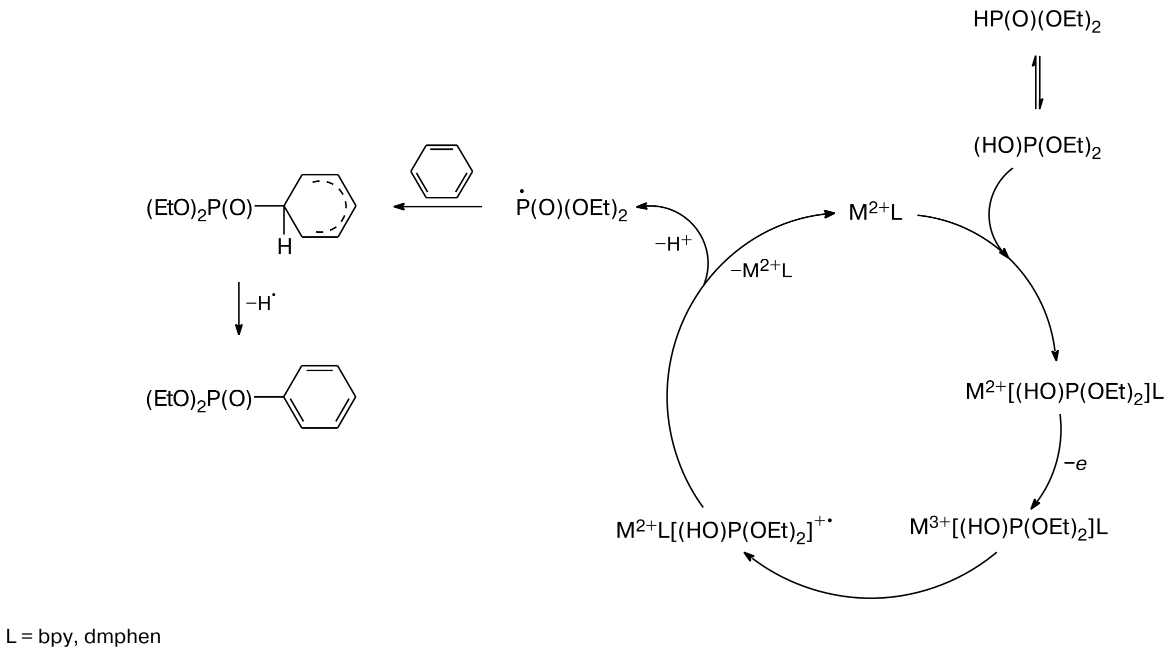
tion of $MnCl_2$bipy is irreversible at a 1.14 V potential. Upon addition of phosphonate $HP(O)(OEt)_2$ to the solution of complex $MnCl_2$bipy, a shift of this peak to the less anodic potentials (0.99 V) is observed, with its slow growth upon increase in the content of the phosphonate in the solution to reach $i_{cat}/i_{dif} = 21$ at the ratio of 1 : 168. The large amounts of diethyl phosphite lead to a quasi-reversibility, as in the case of oxidation of $CoCl_2$bipy and other complexes. However, the addition of benzene to the solution of a mixture of complex $MnCl_2$bipy and phosphite does not lead to the increase in the catalytic current effect (Fig. 6), in contrast to complexes $Ni(BF_4)_2$dmphen, $CoCl_2$dmphen, and $CoCl_2$bipy.

It is probable that the changes in the redox properties of metal complexes observed in the presence of diethyl phosphite are due to the strong coordinating properties of the latter[24,25] and the formation of metal phosphonates, which undergo oxidation at smaller potential than the starting complexes. Preparative electrolysis does proceed at potentials corresponding to the oxidation of phosphonate complexes. The current increasing of complexes observed upon addition of benzene indicates a rapid regeneration of the catalyst active form in such three- and four-component systems. To compare catalytic efficiencies of the systems containing cobalt, nickel, and manganese (or in their absence), we have chosen identical conditions (Table 3, Figs 7 and 8). The high i_{cat}/i_{dif} values (see Table 3) for complex $Ni(BF_4)_2$dmphen in both presence and absence of manganese indicate its higher catalytic activity in the phosphorylation reaction as compared to other systems. This explains the formation of polyphosphorylation

Scheme 2



Scheme 3



products of benzene in the process of electrosynthesis with the nickel complex.

A generalized scheme for the catalytic cycle can be suggested (Scheme 2).

A catalytic scheme involving a mono-component catalyst simplifies (Scheme 3).

In conclusion, a suggested method for the electrosynthesis of diethyl phenylphosphonate proceeds under mild conditions (room temperature, normal pressure) and with 1 : 1 ratio of reagents gives the product in high yield (up to 90%) and 100% conversion in the presence of bimetallic catalytic systems $MnSO_4/CoCl_2$dmphen or $MnCl_2/CoCl_2$bipy. The mechanism of the process requires further studies, but we suppose that the first step of the cycle is probably the formation of the metal (or metals) phosphonate undergoing oxidation at low anodic potentials with elimination of the phosphonate radical, which reacts with benzene.

Experimental

Cyclic voltammetry. Cyclic voltamgrams were recorded using a BASi Epsilon E2P potentiometer (USA). The instrument is composed of a measurement unit and a DellOptiplex 320 personal computer with the Epsilon-EC-USB-V200 program. Tetraethylammonium and tetrabutylammonium tetrafluoroborates were used as supporting electrolytes. A stationary glassy carbon disk (surface area 6 mm^2) served as a working electrode, a reference electrode was Ag/AgCl (0.01 mol L^{-1}), platinum wire served as an auxiliary electrode. CVA curves were recorded at the rates of potential linear sweep of 100 mV s^{-1}. The measurements were carried out in a thermostated (25 °C) electrochemical cell (1—5 mL) under inert atmosphere (N_2).

Before recording CVA curves and between measurements, the solution was vigorously stirred on a magnetic stirrer under inert atmosphere, which was passed first through a drying system and then through a BI-GAScleaner system (Modern Laboratory Equipment, Novosibirsk) for purification from the trace amounts of oxygen.

Preparative electrosynthesis. Preparative electrolysis was carried out using a source of direct current B5-49 in a 40-mL three-electrode cell. The working electrode potential was measured using a V7-27 DC voltmeter relative to the reference electrode Ag/AgCl (0.01 mol L^{-1}) in acetonitrile. The surface of the working platinum U-shaped electrode was 48.00 cm^2. A ceramic plate with 900-nm pores was used as a diaphragm. During preparative synthesis, the electrolyte was continuously stirred with a magnetic stirrer under a constant current of an inert gas, which was passed through the purification system from oxygen and other gases.

NMR spectra were recorded on a Bruker Avance-400 multinuclear spectrometer (400.1 (^{1}H) and 162.0 MHz (^{31}P)) relative to a reference, the signal of the deuterated solvent (^{1}H NMR) or phosphoric acid (^{31}P NMR).

Mass spectrometric studies (ESI-MS analysis) were carried out on an AmazonX instrument (Bruker Daltonik GmbH, Germany), electrospray ionization. Nitrogen was used as a drying gas in the source with temperature 220 °C. The source potential was 4.5 kV. Solutions of the samples were diluted with acetonitrile to the concentration of ~10^{-3} mg mL^{-1}. The samples were injected using an autosampler of the Agilent 1260 Infinity liquid chromatograph (Agilent Technologies, USA).

Reagents and objects of studies. Acetonitrile (Acros Organics, extra purity grade) was used as a solvent in the syntheses, which before use was thrice distilled, first distillation was carried out over potassium permanganate, second distillation over phosphorus pentoxide, and third over calcium hydride under argon.

Diethyl phenylphosphonate was obtained according to the procedure described earlier.[26] Benzene was purified by ordinary distillation over sodium. The purified solvents were stored under inert atmosphere in Schlenk systems.

Tetraethylammonium tetrafluoroborate was obtained by mixing a 30—35% aqueous solution of tetraethylammonium hydroxide and HBF_4 until neutrality shown by indicator. A white crystalline precipitate was formed in the course of the reaction, which was filtered and dried. A resulting powdered salt was recrystallized from ethanol and dried 2—3 days in a drying oven *in vacuo* at 55 °C.

Synthesis of metal complexes (general procedure). A corresponding ligand ($1.83 \cdot 10^{-2}$ mol in ethanol (30—50 mL) was slowly added to a solution of metal salt MX_2 ($1.83 \cdot 10^{-2}$ mol) in the same solvent (100 mL) with stirring. The reaction mixture was stirred at constant temperature (25 °C) for 3—24 h until a crystalline precipitate was formed. the precipitate was filtered under argon and washed with ice-cold ethanol. The complex was dried in a drying oven *in vacuo* for 2—3 days at 25—55 °C. Physicochemical characteristics of the synthesized complexes $CoCl_2$dmphen,[27] $CoCl_2$bipy,[28] $NiBr_2$dmphen, and $NiBr_2$bipy (see Ref. 29) agree with the literature data.

Electrocatalytic phosphorylation of benzene (general procedure). Diethyl phosphite ($1.2 \cdot 10^{-3}$ mol), benzene ($1.2 \cdot 10^{-3}$ mol), and a metal complex MX_2L ($0.12 \cdot 10^{-3}$ mol) in MeCN (40 mL) were placed into a electrochemical cell. Electrolysis was carried out in an electrochemical cell with divided anode and cathode compartments at 23 °C under dry argon in galvanostatic mode with 0.7 V potential on working electrode. The amount of passed electricity was 2 *F* per 1 mol of phosphite. After the electrolysis was complete, the reaction mixture was washed with saturated aqueous ammonium chloride (3×50 mL) and extracted with chloroform (3×70 mL). After separation, the organic layer was dried with magnesium sulfate, the solvent was evaporated, the residue was purified by passing through a chromatographic column with silica gel (eluent ethyl acetate—hexane). Physicochemical and spectral characteristics of the product (diethyl phenylphosphonate) agree with the literature data.[30] When $Ni(BF_4)_2$dmphen was used as a catalyst, the phosphorylation products were benzene polyphosphonates isolated as a mixture: $[M + H]^{+\bullet} = 894.22$ ($C_{30}H_{60}O_{18}P_6$); $[M + H]^{+\bullet} = 758.91$ ($C_{26}H_{51}O_{15}P_5$); $[M + H]^{+\bullet} = 622.74$ ($C_{22}H_{42}O_{12}P_4$); $[M + H]^{+\bullet} = 486.60$ ($C_{18}H_{33}O_9P_3$); $[M + H]^{+\bullet} = 350.53$ ($C_{14}H_{24}O_6P_2$).

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