Cu^I complexes with 2,2´-biquinolyl-containing polymeric ligands as electrocatalysts for the oxidative coupling of alkynes in the presence of dioxygen

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Electrocatalytic oxidative coupling of terminal alkynes in the presence of atmospheric oxygen catalyzed by Cu^I complexes with polymeric biquinolyl ligands leads to the corresponding diynes in high yield. The reaction proceeds under mild conditions at a potential of Cu^{II}/Cu^I electroreduction (−0.55 V *vs.* Ag/AgCl/KCl) and is accompanied by O_2 reduction to H_2O.

Key words: copper-containing polymers, biquinolyl complexes, electrocatalysis, oxidative coupling, alkynes, dioxygen.

The Cu^I complexes with N-containing ligands are known to catalyze various aerobic oxidative processes including biochemical reactions (see, *e.g.*, Refs 1—3 and papers cited therein). The structures of Cu/O_2 complexes formed during the reactions were investigated in detail.[4] It was demonstrated that they depend strongly on the Cu ion coordination environment and determine largely the type of the catalytic process. The range of oxidative processes involving molecular oxygen is very wide.[4] Oxidative aerobic coupling of terminal alkynes catalyzed by Cu complexes is an example. The interest in such a process is, in particular, due to the fact that the polyyne systems are widely used in preparation of molecular wires, luminescent materials, *etc.*[5]

Oxidative coupling of alkynes is usually performed using Cu^{II} complexes with amine-containing ligands. The yield of the dimer and the reaction rate strongly depend on the nature of the alkyne, as well as on the ligand type.[6—10] A comparison of the catalytic efficiency of dendrimeric amine-containing copper complexes with that of their low-molecular-weight analogs revealed the advantages of the former, which seems to be related to the better complexing ability and to the increase in the local concentration of the reagents due to the adsorption of the alkyne molecule on the dendrimer surface.[11] Recently,[12] a detailed quantum chemical investigation (DFT computation) of the mechanism of the oxidative coupling of alkynes in the presence of atmospheric oxygen has been published. It revealed that the key step of the process might be the oxidation of copper acetylenide formed with dioxygen yielding a binuclear $[Cu_2(\mu\text{-}O_2]^{2+}$ dioxo-complex. The energy profile has been calculated; the obtained small values of the activation energy nicely correspond to the fact that the reaction proceeds at room temperature.

The electrocatalytic coupling of alkynes in the presence of atmospheric oxygen has not been investigated so far. Furthermore, electrochemical activation allows performing reactions under mild conditions, at room temperature and atmospheric pressure, which often ensures high selectivity of a process.[13]

Recently,[14] we have elaborated an electrochemical approach using the sacrificial anode technique to the new polynuclear Cu^I complexes with polymeric ligands based on polyamido acids (PA) with biquinolyl (biQ) fragments in the polymer backbone. The presence of the polymeric ligand, as well as the presence of the excess of Cu^I ions (which is easily accessible using instrumental control by optimization of the current and potential values) allow one to obtain coordinatively unsaturated Cu^I complexes with only one biQ fragment in the Cu^I coordination environment.

These complexes appeared to be capable of activating molecular oxygen. They showed high electrocatalytic activity in the aerobic oxidation of aliphatic alcohols to the corresponding carbonyl derivatives.[15] As follows from the experimental results, the polymeric chain stabilizes coordinatively unsaturated Cu^I complexes ($[Cu(PA)L_2]BF_4$) that are catalytically active. Especially high catalytic activity can be achieved when using polymer Cu^I complexes immobilized on a graphite electrode.[15]

In continuation of this research, we studied the applicability of the above-mentioned polymeric biquinoline

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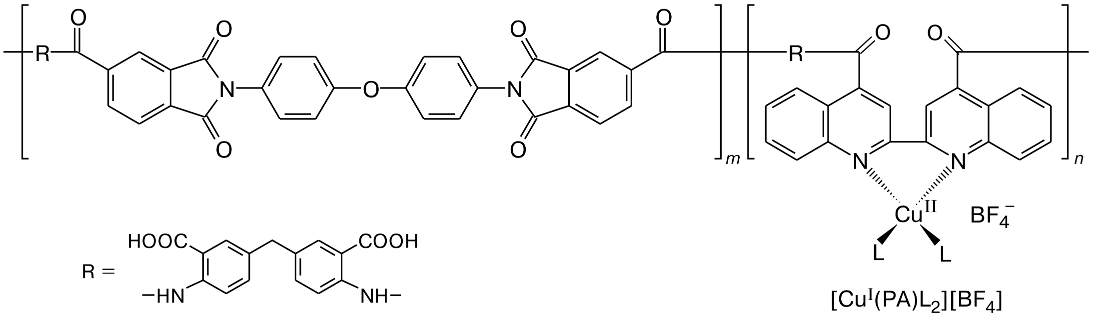


$[Cu^I(PA)L_2][BF_4]$

m : *n* = *8* : *2*; L are the molecules of the solvent (*N*-methylpyrrolidone, MeCN)

Cu^I complexes as catalysts for oxidative dimerization of terminal alkynes in the presence of atmospheric oxygen under conditions of electrochemical activation.

Experimental

Acetonitrile (pure grade) was stirred with CaH_2 for 12 h and distilled, then refluxed for 2 h over P_2O_5 and distilled again collecting the fraction with b.p. 81—82 °C (760 Torr).

Preparative electrolysis was performed with a P-5827M potentiostat in an undivided 10 mL electrochemical cell. The working electrode was graphite fabric with immobilized $[Cu^I(PA)L_2]BF_4$ complex (see Refs 14, 15), the counter electrode was a platinum plate. All potentials are referred to Ag/AgCl/KCl aq. reference electrode (the potential versus Fc/Fc^+ in acetonitrile is about −0.43 V). The measured potential values were recalculated considering ohmic drops.

GC-MS analysis of the reaction mixtures was carried out with the GC-MS spectrometer Finnigan MAT SSQ 7000 with ionization energy of 70 eV, with capillary silicon column HP-5 (30 m). Detector and injector temperatures were 50 °C.

Electrocatalytic coupling of alkynes with O_2 in the presence of $[Cu^I(PA)L_2]BF_4$ immobilized on the graphite electrode. The electrolysis was performed in a potentiostatic regime at a potential of −0.55 V in the cell equipped with the efficient reflux condenser filled with ice water. An alkyne (0.1 mmol) was dissolved in 10 mL of MeCN (5% H_2O) containing 132 mg of Bu_4NBF_4 (0.05 mol L^{-1}). A 1 : 1 mixture of argon and air was bubbled through the solution (24 mL min^{-1}) during the electrolysis. The process was stopped after 2 *F* mol^{-1} of charge was passed (19.6 C per starting alkyne). The obtained solution was analyzed using GC-MS. The peaks of molecular ions were observed in all cases, m/z (I_{rel} (%): 202 $[M]^+$ (100) (PhC≡C—C≡CPh); 106 $[M]^+$ (100), 91 $[M^+-CH_3]$ (80), 76 $[M^+-2\ CH_3]$ (38) (PrC≡C—C≡CPr); 194 $[M]^+$ (20), 179 $[M^+-CH_3]$ (100) (Me_3Si—C≡C—C≡C—$SiMe_3$).

The yield of the reaction products was estimated by GC-MS using mesitylene as the standard.

Results and Discussion

Three types of terminal alkynes were chosen for investigation: with an aryl, alkyl, and element-containing substituent at the C≡C triple bond, *viz.*, phenylacetylene, pent-1-yne, and trimethylsilylacetylene. All these compounds were found to undergo dimerization when the proposed[14] catalytic system was used. The reaction proceeds at a low cathodic potential (−0.55 V) at room temperature and atmospheric pressure of air. This potential value has been demonstrated[14] to correspond to the Cu^{II}/Cu^I redox-transfer providing formation of the active form of the catalyst. Direct electrochemical dioxygen reduction on a Pt electrode in acetonitrile proceeds at a potential of −1.1 V.[16] When the Cu-polymer is immobilized on the graphite electrode, an intensive increase in the Cu^{II}/Cu^I reduction current at a potential of −0.55 V is observed in acetonitrile depending on the O_2 concentration. This suggests the electroactivity of Cu^I-complex with respect to O_2 and electrocatalytic O_2 reduction in the presence of the Cu-polymer.

The oxidative coupling of alkynes was performed in the undivided electrochemical cell in MeCN using the polymeric complex $[Cu(PA)L_2]BF_4$ immobilized on the graphite electrode surface as a catalyst.[14] The flow of air was passed through the electrochemical cell. As follows from Table 1, the coupling of all three investigated compounds occurs with the high yield and current efficiency.

As one can see in Table 1, the yields of the dimers are somewhat lower in the case of pent-1-yne and trimethylsilylacetylene, as compared with phenylacetylene, probably, due to their volatility. Special measures to minimize evaporation of the starting alkynes during the experiment were undertaken (see Experimental), but it was not possible to avoid losses completely. Chromatographic (GC-MS and GC) analysis of the reaction mixtures showed the presence of the dimers only, without even traces of the starting alkynes. This allows one to make a conclusion that the catalytic cycle provides the complete conversion of the alkyne to diyne and the decrease in the yield is attributed to the partial losses of the starting alkynes due to their evaporation in the air flow.

The amount of the employed catalyst ($[Cu(PA)L_2]BF_4$) is $3.2 \cdot 10^{-8}$ mol (0.032 mol.%) relative to the starting alkyne. The application of the cathodic potential that corresponds to Cu^{II}/Cu^I redox-transition is necessary for regeneration of the catalyst and for the accomplishment of the catalytic cycle. Control experiments demonstrated that no reaction occurs when the electrochemical cell is switched off.

Table 1. The yield and current efficiency of electrocatalytic oxidative coupling of alkynes (0.1 mmol) in MeCN : H_2O = 20 : 1 in the presence of the catalyst ($3.2 \cdot 10^{-8}$ mol) at a potential of −0.55 V (*vs.* Ag/AgCl/KCl)

Substrate	Product	Yield (%)	
		by current	by substance
PhC≡CH	PhC≡C—C≡CPh	81	81
PrC≡CH	PrC≡C—C≡CPr	63	66
$Me_3SiC≡CH$	$Me_3SiC≡C—C≡CSiMe_3$	75	77

Reduction of dioxygen in the catalytic cycle is known[16] to proceed with formation of either H_2O_2 (the consumption of two electrons) or H_2O (the consumption of four electrons). The cyclic voltammetry investigation of the solutions obtained after electrolysis showed no even traces of hydrogen peroxide, which could be detected by its characteristic reduction peak at a potential of −1.29 V (see Ref. 16). The application of the chemical tests (*e.g.*, with KI) also gave a negative result. Consequently, four-electron reduction of O_2 to water does occur in the investigated catalytic cycle, thus making the reaction ecologically friendly.

The formal reaction stoichiometry can be presented as follows:

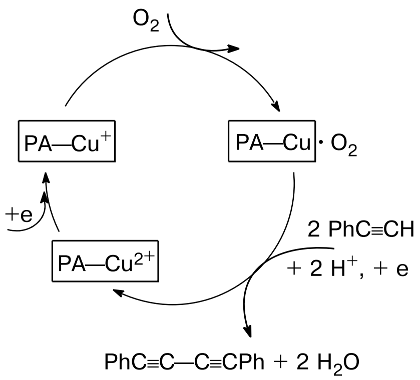
$$\mathrm{Cu^+ + O_2 + 2\ RC{\equiv}CH + e^- + 2\ H^+ \rightarrow}$$
$$\mathrm{\rightarrow Cu^{2+} + RC{\equiv}C{-}C{\equiv}CR + 2\ H_2O.}$$

Four electrons, which are necessary for the reduction of dioxygen to water, are supplied by the molecules of the alkyne that is oxidized (two electrons per two molecules of alkyne) and the electrode (due to the Cu^{II}/Cu^{I} reduction and the regeneration of the catalyst). Water is the source of additional protons. Special experiments showed that the process does not occur (the current value is zero) in thoroughly dried acetonitrile and when the air specially dried by passing through the vessel with concentrated H_2SO_4 is bubbled through the cell.

The elucidation of the reaction mechanism is not a subject of the present study. However, based on literature data,[12,17] an active Cu^{I} complex with molecular oxygen can be assumed to serve as an oxidant. Unfortunately, we were not able to determine the type of the oxygen-containing adduct. The reason for that was the immobilization of the catalyst on the graphite electrode, which makes impossible the registration of the electronic absorption spectra, which usually serve as a major diagnostic criterion[4] of the structure of the intermediate. The realization of the catalytic cycle involving the peroxide anion[18] might be considered as an alternative mechanism but, as it has been showed earlier,[14,15] in the presence of copper complexes this route seems to be unlikely.

The catalytic cycle in shown in Scheme 1.

Scheme 1



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