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Organic Electron Carriers in the Electrochemical Synthesis of Metal Carbonyls

Vitalii V. Yanilkin,[a*] Bulat M. Garifullin,[b] Farid F. Nigmadzhanov,[a] Zoya S. Titova,[a] and Yurii M. Kargin[b]

[a] *A. E. Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences, 420083 Kazan, Russian Federation. Fax: +7 8432 75 2253*

[b] *Department of Physical Chemistry, Kazan State University, 420008 Kazan, Russian Federation.*

Homogeneous reduction of Ni^{II}, Fe^{II} and Co^{II} ions by anion-radicals of organic compounds in the presence of carbon monoxide, in a mixture of acetonitrile and benzene (3:1) under normal conditions, leads to metal carbonyls (Ni, Fe) and carbonyl metal anions (Co).

Recently[1,2] we have observed a considerable acceleration of homogeneous electrochemical reduction of gem-dichlorocyclopropanes by anthracene anion-radicals in the presence of nickel and cobalt ions. In addition, it was supposed that in this two-component system the homogeneous electron transfer stage from anion-radical to metal ion takes place with the formation of either metal ion in the lower oxidation state as intermediate or a metal in the zero oxidation state. This intermediate then interacts with halogenoorganic compounds. The detection of these intermediates or products of their transformation is significant in revealing the mechanism of the processes in the two-component system, and can be of some interest itself. In this connection we have studied the possibility of formation of metal carbonyls in homogeneous metal-ion reduction by organic mediators in the presence of carbon monoxide.

The process was carried out at 12 °C in MeCN–benzene (3:1) containing 0.1 mol dm^{-3} tetrabutylammonium bromide in the undivided cell. To release dissolved oxygen and to saturate the solution with carbon monoxide, the latter was allowed to pass through the solution before electrolysis during 30 min and then during the whole electrolysis process under atmospheric pressure. The lead cylinder $S = 15$ cm^2 was used as a cathode. Metal ions were delivered into the solution directly by ‘anodic dissolution’ of the corresponding metal during electrolysis. The process of organic compound reduction to form the anion-radicals–the homogeneous redox reaction by which the metal ions might lead to the formation of the metal carbonyls (Ni, Fe) or carbonyl metal anion (Co)–takes place on the cathode. Side by side with these processes is a possible reduction of metal ions on the electrode.

Table 1 The results of galvanostatic electrolysis of condensed arenes in the system with a soluble anode in the presence of CO ($I = 0.3$ A, $P_{CO} = 1$ bar, $T = 12$ °C).

Organic carrier	Anode	Amount of electricity/F	Electrolysis product (ν_{CO}/cm^{-1})	Yield[a] (%)
Anthracene	Ni	0.07	$Ni(CO)_4$ (1960–2060)	⩾50
Anthracene	Co	0.02	$[Co(CO)_4^-]$ (1900–2050)	⩾80
Anthracene	Fe	0.03	$Fe(CO)_5$ (1980–2050)	⩾40
Naphthalene	Fe	0.03	$Fe(CO)_5$ (1980–2050)	⩾40

[a] Based on the amount of anodically-dissolved metal.

Control over the electrochemical process was achieved spectrophotometrically. IR spectra of the electrolyte were recorded before the electrolysis and during the electrochemical synthesis in the metal carbonyl absorbation range.[3] The frequency range ν_{CO} observed by us, conditions and data for the electrolysis are summarized in Table 1. As seen in Table 1 the formation of carbonyl metal derivatives in sufficiently high yield was detected in the presence of organic carriers. The results presented here confirm that in the two-component system described above either metal ions in a lower oxidation state or metal in the zero oxidation state were formed. These are presumably involved in the process of metal carbonyls formation under mild conditions.

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