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Calculation of the Possibility of Formation of a Cyclic Metallolactone Anionic Complex in the Methyloxirane–Potassium Tetracarbonylcobaltate System

V. P. Boyarskii[a], I. A. Boyarskaya[a], and G. G. Duka[b]

[a] *St. Petersburg State University, Universitetskii pr. 26, St. Petersburg, 198504 Russia*
e-mail: vadimpb@yahoo.com

[b] *Moldavian Academy of Sciences, Kishinev, Moldova*

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Abstract—The reaction of the tetracarbonylcobaltate anion with methyloxirane was studied by quantum-chemical methods to show that a metallocyclic complex is energetically preferred over an alkylcobaltcarbonyl one.

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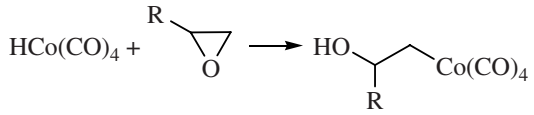
The formation of alkylcarbonylcobalt complexes **I** in the reaction of cobalt hydrocarbonyl with oxiranes has first been described in 1963 [1] (Scheme 1).

Scheme 1.

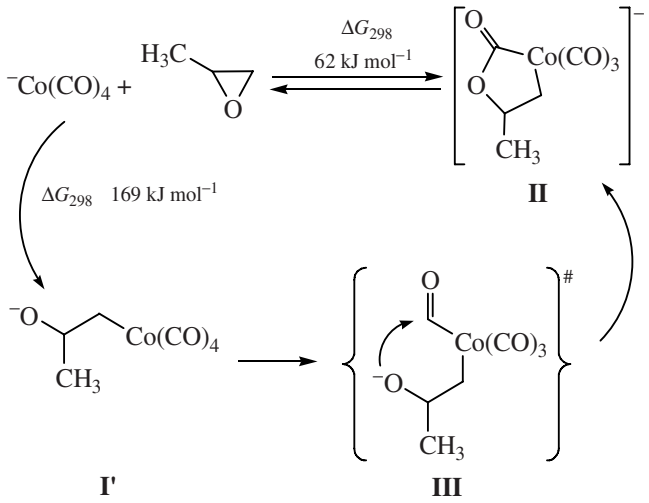


I

These complexes are intermediate products in the synthesis of β-lactones by carbonylation of epoxides [2–4], as well as effective catalysts of carbonylation of aryl halides basic alcohol media (in the form of anions) [5–7]. However, the nature of complexes **I** has scarcely been explored. A recent mechanistic study of the carbonylation of aryl halides in a catalytic system comprising cobalt carbonyl, monoalkyloxirane, and base showed that this catalytic system activates aryl halides by the radical ion mechanism [8]. Therewith, based on kinetic and IR spectral data, the referees concluded that the active catalytic complex is formed irreversibly and suggested that the compex has a cyclic structure **II** rather than open-chain (structure **I'** or **III**) (Scheme 2).

It the present work we have studied the reaction of the tetracarbonylcobaltate anion with methyloxirane in

Scheme 2.



methanol by means of DFT/B3LYB–6-31+G(d,p) (Gaussian 03 [9]) calculations. Four possible stable states of the system were calculated: ground state as a combination of two species: tetracarbonylcobaltate and methyloxirane, as well as complexes **I'**, **II**, and **III**. The calculations were performed both without inclusion and with inclusion of solvation by the polarized continuum model (PCM) [10].

According to the calculation results, states **I'** and **II** correspond to potential energy minima, whereas the *cisoid* form of the open-chain hydroxyalkylcarbonylcobaltate anion has an imaginary frequency and, consequently, can function exclusively as a transition

state on the cyclization of the *transoid* form of complex **I'** into anionic metallocyclic complex **II**.

It was also found that complex **II** is much lower by energy than complex **I'**. The energy gap (with zero-point correction) was $\Delta E_{\mathbf{I'-II}}$ 142 kJ mol^{-1} in a vacuum and 112 kJ mol^{-1} with a PCM solvation correction. These data provide evidence for our previous suggestion [8] that the catalytic complex formed in the cobalt-catalyzed carbonylation of aryl halides has a cyclic metallolactone structure.

Comparison of the Gibbs energies of the ground state and catalytic complex **II** ($\Delta G_{\mathbf{II}-\text{init}}$ 62 kJ mol^{-1} at 25°C) allows us to conclude that in the case in hand the equilibrium we found in [8] for the cobalt-catalyzed carbonylation of aryl halides is strongly shifted to the initial state. This conclusion is consistent with the finding in [8] that for the maximum activity of the catalytic system a considerable excess of methyloxirane should be used.

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