Russian Journal of General Chemistry, Vol. 74, No. 11, 2004, pp. 1766–1769. Translated from Zhurnal Obshchei Khimii, Vol. 74, No. 11, 2004, pp. 1898–1901.

Influence of the Structure of the Macroheterocyclic Ligand on the Catalytic Properties of Metal Tetraarenoporphyrazine Complexes: III.[1] Oxidative Decarboxylation of Oxalic Acid

A. B. Korzhenevskii, T. G. Shikova, O. I. Koifman, and V. V. Bykova

Ivanovo State University of Chemical Engineering, Ivanovo, Russia
Ivanovo State University, Ivanovo, Russia

Received March 13, 2003

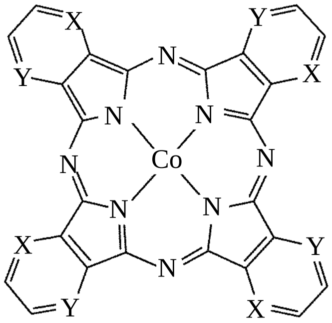
Abstract—The catalytic activity of cobalt complexes of a series of tetraarenoporphyrazines in oxidative decarboxylation of oxalic acid under heterogeneous conditions was studied. The structure of the macroheterocycle exerts a significant effect on the catalytic properties of the metal complexes.

Metal phthalocyanines catalyze oxidation of various organic substances, in particular, of carboxylic acids. Their activity in oxidation of formic acid [2–6] and in decarboxylation of pyruvic and oxalic acids [7, 8] was studied previously. It was found that oxalic acid in the presence of iron phthalocyanine decomposes at a rate exceeding by a factor of 7 the rate of decarboxylation of pyruvic acid under the same conditions. Therefore, oxidative decarboxylation of oxalic acid was suggested as a test reaction in evaluation of the catalytic properties of phthalocyanines [7]:

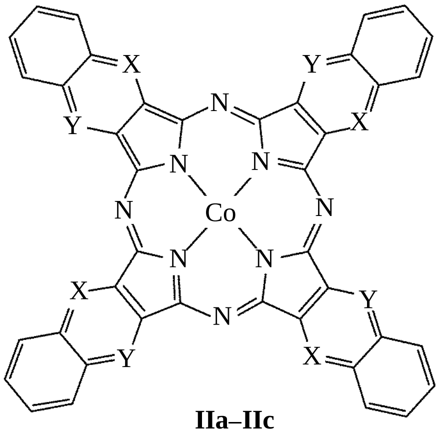
$$\mathrm{HOOC{-}COOH} + 1/2\mathrm{O_2} \longrightarrow \mathrm{H_2O} + 2\mathrm{CO_2}.$$

To reveal how the structure of the macrocyclic ligand affects the catalytic properties of the cobalt complexes in oxidative decarboxylation of oxalic acid, we studied the catalytic activity of the cobalt complexes of tetra-2,3-pyridinoporphyrazine (2,3-PycCo, **Ib**), tetrapyrazinoporphyrazine (PzcCo, **Ic**), 2,3-naphthalocyanine (2,3-NcCo, **IIa**), tetra-2,3-quinolinoporphyrazine (2,3-QlcCo, **IIb**), and tetra-2,3-quinoxalinoporphyrazine (2,3-QxcCo, **IIc**), in comparison with that of cobalt phthalocyanine (PcCo, **Ia**).

It was found previously [9] that the mechanisms of catalytic oxidation of cysteine and oxidative decarboxylation of oxalic acid in the presence of metal phthalocyanines are similar, and, under the conditions of a heterogeneous catalytic reaction, the first step is formation of a catalyst–substrate complex. Hence, adsorption of oxygen is preceded by extra coordination of oxalic acid with the metal ion, and oxidation of oxalic acid occurs in the ternary adsorption complex.



Ia–Ic



IIa–IIc

I, II, X = Y = CH (**a**), N (**c**); X = CH, Y = N (**b**).

Extra coordination of anions with the central metal atom of phthalocyanine complexes is well known

---

[1] For communication II, see [1].

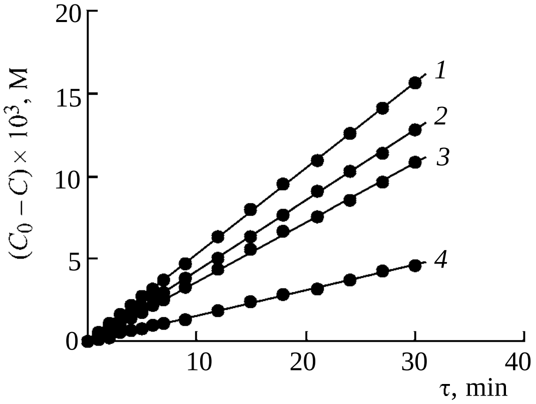


Fig. 1. Kinetic curves of catalytic oxidative decarboxylation of oxalic acid at 513 K in the presence of cobalt tetraazaporphyrazines: (*1*) [PcCo] 20.31×10^{-4} M, (*2*) [2,3-PycCo] 22.68×10^{-4} M, (*3*) [2,3-NcCo] 6.02×10^{-4} M, and (*4*) [PzcCo] 19.08×10^{-4} M.

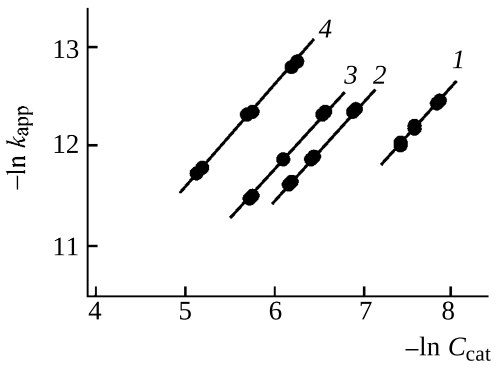


Fig. 2. Plot of $\ln k_{app}$ vs. $\ln C_{cat}$ in oxidative decarboxylation of oxalic acid at 313 K in the presence of (*1*) 2,3-NcCo, (*2*) PcCo, (*3*) 2,3-PycCo, and (*4*) PzcCo.

[10]. Furthermore, preliminary extra coordination of electron-donor molecules on the cobalt and iron ions in the corresponding metal porphyrins facilitates the subsequent complexation of the extra complexes with oxygen [11].

Borisenkova *et al.* [8] found that the rate of decarboxylation of oxalic acid in the presence of metal phthalocyanines is directly proportional to the amount of the catalyst and is independent of the concentration of the reacting acid within the range from 0.7 to 1.6 M. Based on the general concepts of chemical kinetics, the equation for the reaction rate will be as follows:

$$-dC_{oa}/d\tau = k_v C_{oa}^m C_{cat}^n C_{ox}^p \text{ or } -dC_{oa}/d\tau = k_{app} C_{oa}^m,$$

where C_{oa} is the oxalic acid concentration; C_{cat}, conventional molar concentration of the catalyst; C_{ox}, oxygen concentration; k_v and k_{app}, true and apparent rate constants; m, n, and p, reaction orders with respect to the corresponding components.

It was found by the Whinkler method that the oxygen concentration in the reaction zone was constant in the course of the experiment, 1.05×10^{-3} M, which was provided by approximately constant composition and pressure of the gas mixture and efficient transfer of oxygen from the gas phase to water.

The results of the previous studies of this test reaction allowed us to choose the optimal reaction conditions: aqueous solution, oxalic acid concentration 0.8 M, 40–60°C, catalyst concentration range 1×10^{-4}–5×10^{-3} M.

We found that the rection is zero-order with respect to the substrate in the presence of all the tested metal complexes (Fig. 1), which is consistent with published data [8]. From the kinetic dependences obtained, we calculated the apparent rate constants (k_{app}) and estimated the reaction order with respect to the conventional molar concentration of the catalyst (C_{cat}) (Fig. 2); in all the cases, it was unity.

Comparison of the reaction orders with respect to the substrate and catalyst in the presence of PcCo and the other metal complexes studied suggests that the reaction mechanism is similar with all the cobalt tetraarenoporphyrazines.

The constants k_v found from k_{app}, C_{cat}, and C_{ox} assuming that the reaction order with respect to oxygen is unity (by analogy with the reaction mechanism in the presence of MPc [8]) can be used for comparing the catalytic activity of the compounds and for calculating the activation energy and entropy of the reaction.

Our experimental data and calculation results characterizing the kinetics of the process studied are given in the table. These data show that the catalytic activity of the metal complexes in oxidative decarboxylation of oxalic acid decreases in the order 2,3-NcCo > PcCo > 2,3-PycCo > PzcCo. The cobalt complexes of tetra-2,3-quinolinoporphyrazine and tetra-2,3-quinoxalinoporphyrazine appeared to be inactive in this reaction.

The activation parameters for all the cobalt tetraarenoporphyrazines studied demonstrate a compensation effect (Fig. 3), confirming that the reaction mechanism is similar irrespective of the structure of the macroheterocycle. Hence, the mechanism suggested

Catalytic activity of cobalt complexes of phthalocyanine and its structural analogs in oxidative decarboxylation of oxalic acid[a]

T, K	$C_{cat} \times 10^4$, M	$k_{app} \times 10^6$, mol l^{-1} s^{-1}	k_v, l s^{-1} mol^{-1}
		PcCO	
313	9.81	4.23 ± 0.04	4.11
	16.37	7.05 ± 0.04	4.09
	20.31	8.74 ± 0.04	4.10
323	7.09	5.88 ± 0.04	7.90
	11.12	9.29 ± 0.04	7.95
	13.92	11.61 ± 0.03	7.94
333	5.78	9.00 ± 0.04	14.84
	8.58	13.28 ± 0.05	14.74
	10.77	16.73 ± 0.07	14.79
		2,3-PycCo	
313	13.82	4.30 ± 0.03	2.96
	22.68	7.09 ± 0.03	2.96
	33.02	10.30 ± 0.03	2.97
323	7.04	4.39 ± 0.01	5.94
	11.99	7.53 ± 0.03	5.98
	19.29	12.10 ± 0.04	5.97
333	4.43	5.37 ± 0.04	11.55
	7.13	8.66 ± 0.04	11.57
	11.82	14.32 ± 0.04	11.54
		PzcCo	
313	19.08	2.59 ± 0.03	1.29
	33.25	4.52 ± 0.02	1.29
	59.15	8.05 ± 0.04	1.29
323	17.01	4.92 ± 0.04	2.75
	25.99	7.51 ± 0.03	2.75
	34.80	10.05 ± 0.03	2.75
333	8.81	5.17 ± 0.04	5.59
	14.59	8.54 ± 0.03	5.57
	22.28	13.03 ± 0.03	5.57
		2,3-NcCo	
313	3.89	3.88 ± 0.04	9.50
	5.05	5.10 ± 0.03	9.54
	6.02	6.01 ± 0.05	9.50
323	2.39	4.29 ± 0.04	17.07
	3.49	6.23 ± 0.03	16.96
	4.99	8.88 ± 0.03	16.97
333	1.55	4.99 ± 0.03	30.63
	2.27	7.26 ± 0.04	30.51
	3.24	10.40 ± 0.03	30.60

[a] PcCo: $E^{\neq}$ 55 kJ mol^{-1}, $\Delta S^{\neq}$ −64 J K^{-1} mol^{-1}; 2,3-PycCo: $E^{\neq}$ 59 kJ mol^{-1}, $\Delta S^{\neq}$ −56 J K^{-1} mol^{-1}; PzcCo: $E^{\neq}$ 63 kJ mol^{-1}, $\Delta S^{\neq}$ −48 J K^{-1} mol^{-1}; 2,3-NcCo: $E^{\neq}$ 51 kJ mol^{-1}, $\Delta S^{\neq}$ −73 J K^{-1} mol^{-1}. The error in calculating $E^{\neq}$ and $\Delta S^{\neq}$ is 10%.

for oxidative decarboxylation of oxalic acid catalyzed with PcCo can be applied to the processes occurring in the presence of the other cobalt complexes studied.

As in catalytic decomposition of hydrogen peroxide [12] and oxidation of cysteine [1], the structure of the macroheterocyclic ligand appreciably affects the catalytic properties of the metal complexes. In particular, aza substitution at the molecular periphery decreases the rate of the catalyzed reaction, and benzannelation exerts a differentiating effect on the catalytic activity, enhancing that of the phthalocyanine and suppressing that of its aza analogs.

It was found previously that introduction of electron-withdrawing substituents into the phthalocyanine molecule also decreases the catalytic activity of its metal complexes [13]. In this study we observed a similar trend.

Apparently, the catalytic activity of metal tetraarenoporphyrazine complexes in oxidative decarboxylation of oxalic acid, determined, in particular, by their capability for extra coordination of the anion, is very sensitive to variation of the electron density on the metal atom, caused by introduction of substituents into the macrocyclic ligand.

The remote periphery exerts a strikingly strong effect on the catalytic activity of metal complexes of tetraarenoporphyrazines in decarboxylation: benzannelation of the secondary conjugation contours enhances the activity of cobalt phthalocyanine but fully deactivates cobalt tetra- and octaazaphthalocyanines. It is even more surprising that benzannelation differently affects similar reactions of catalytic (in the presence of cobalt tetraarenoporphyrazines) oxidation of oxalic acid and cysteine. In the latter case, the catalytic activity of the complexes increases upon benzannelation,

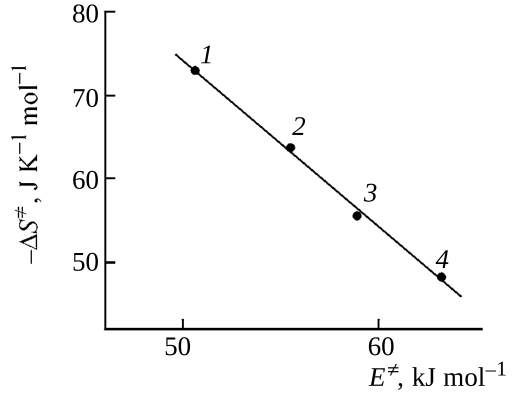


Fig. 3. Compensation effect in oxidative decarboxylation of oxalic acid in the presence of (*1*) 2,3-NcCo, (*2*) PcCo, (*3*) 2,3-PycCo, and (*4*) PzcCo.

irrespective of aza substitution on the ligand periphery [1]. This dualism is hardly attributable to the purely electronic effects of benzannelation. Most probably, the electronic and geometric factors act in opposite directions and exert competing effects on the catalytic activity.

EXPERIMENTAL

The catalytic properties of metal complexes were studied by published procedure [8] using a temperature-controlled rocker. The substrate conversion was monitored by the volume of CO_2 evolved. The experiments were performed at 313–333 K.

The metal complexes of tetraarenoporphyrazines were prepared and purified according to [14–16] and identified on the basis of spectral characteristics [14–16]. Before use, the catalyst samples were treated with water until the wash waters became neutral and free of sulfates, dried to constant weight at 423 K, and thoroughly ground.

REFERENCES

1. Korzhenevskii, A.B., Shikova, T.G., Bykova, V.V., and Koifman, O.I., *Zh. Obshch. Khim.,* 2003, vol. 73, no. 8, p. 1390.
2. Hanke, W., *Z. Chem.,* 1969, vol. 9, no. 1, p. 1.
3. Roginskii, S.Z. and Sakharov, M.M., *Zh. Fiz. Khim.,* 1968, vol. 42, no. 6, p. 1331.
4. Hanke, W., *Z. Anorg. Allg. Chem.,* 1966, vol. 343, no. 3, p. 121.
5. Hanke, W., *Z. Anorg. Allg. Chem.,* 1966, vol. 347, nos. 1–2, p. 67.
6. Tanako, S., Onishi, T., and Tamari, K., *Bull. Chem. Soc. Jpn.,* 1968, vol. 41, no. 11, p. 2557.
7. Borisenkova, S.A., Il’ina, L.M., and Rudenko, A.P., *Vestn. Mosk. Gos. Univ., Ser. 2: Khim.,* 1972, vol. 13, no. 2, p. 249.
8. Borisenkova, S.A., Il’ina, L.M., Leonova, E.V., and Rudenko, A.P., *Zh. Org. Khim.,* 1973, vol. 9, no. 9, p. 1827.
9. Borisenkova, S.A., Denisova, E.P., and Danilova, T.A., *Vestn. Mosk. Gos. Univ.,* Available from VINITI, no. 1802-79.
10. Lever, A.B.P., *Adv. Inorg. Chem. Radiochem.,* 1965, vol. 7, p. 27.
11. Bayer, E. and Schretzmann, P., *Struct. Bonding,* 1967, vol. 2, pp. 181–250.
12. Korzhenevskii, A.B., Shikova, T.G., Bykova, V.V., and Koifman, O.I., *Zh. Obshch. Khim.,* 2002, vol. 72, no. 7, p. 1202.
13. Borisenkova, S.A., Erokhin, A.S., Novikov, V.A., and Rudenko, A.P., *Zh. Org. Khim.,* 1975, vol. 11, no. 9, p. 1977.
14. Markova, L.V., *Cand. Sci. (Chem.) Dissertation,* Ivanovo, 1991.
15. Korzhenevskii, A.B., *Cand. Sci. (Chem.) Dissertation,* Ivanovo, 1977.
16. Bykova, V.V., *Cand. Sci. (Chem.) Dissertation,* Ivanovo, 1981.