ISSN 1070-3632, Russian Journal of General Chemistry, 2006, Vol. 76, No. 5, pp. 822–825. © Pleiades Publishing, Inc., 2006.
Original Russian Text © A.B. Korzhenevskii, S.V. Efimova, A.A. Zelenov, O.I. Koifman, 2006, published in Zhurnal Obshchei Khimii, 2006, Vol. 76, No. 5, pp. 858–861.

Metal Complexes of Polymeric Tetrapyrazinoporphyrazine of the Network Structure: III.[1] Catalytic Properties

A. B. Korzhenevskii[a], S. V. Efimova[b], A. A. Zelenov[b], and O. I. Koifman[a]

[a]Institute of Chemistry of Solutions, Russian Academy of Sciences,
ul. Akademicheskaya 1, Ivanovo, 153045 Russia
[b]Ivanovo State University of Chemical Engineering, Ivanovo, Russia

Received November 8, 2005

Abstract—The catalytic properties of complexes of network polytetrapyrazinoporphyrazine with Cu^{2+}, Co^{2+}, and Fe^{2+} in the decomposition of hydrogen peroxide under heterogeneous conditions were studied. These compounds exhibit catalytic activity which depends on the nature of a metal ion. A comparison of the catalytic properties of the monomeric and polymeric isometallic complexes of tetrapyrazinoporphyrazine reveals an activating effect of the giant conjugated system of the polymeric macroligand.

DOI: 10.1134/S1070363206050264

Metal coordination compounds with complex macrocyclic ligands containing a large closed π-conjugated system, including metal complexes of tetraarenoporphyrazines, are being actively studied with the aim to develop effective catalysts and electrode materials. Long-term studies of catalytic properties of such compounds, in particular, phthalocyanine [2], resulted in the development of a series of effective catalysts [3–5]. By varying the nature of the central metal ion and introducing various substituents into benzene rings of phthalocyanine, it was found that the catalytic activity of metal tetraarenoporphyrazines is largely influenced by both the nature of the metal [6] and the structure of the ligand [7]. The catalytic activity can be considerably enhanced by profound modification of the ligand structure, namely, by introduction of heteroatoms into the ligand periphery and/or its benzannelation [8, 9].

It is interesting to study how the catalytic properties of metal tetraarenoporphyrazines are influenced by their fusion into a macromolecule with continuous π conjugation, i.e., by passing to metal complexes of polytetraarenoporphyrazines.

By now, the effect of such fusion was studied only for a series of metal polyphthalocyanines as applied to hydrogen peroxide decomposition [10–13]. It was found that the catalase activity can increase (for Cu complexes), remain the same (for Ru complexes), or decrease (for Os complexes). The reaction is second-order with respect to the substrate; the order with respect to the catalyst monomeric unit varies from unity (for Cu complexes) to 1.66 (for Ru polyphthalocyanine) [12].

However, there are still no data on the catalytic properties of metal complexes of polymeric tetra(heteroareno)porphyrazines, in particular, of phthalocyanines octaaza-substituted on the periphery, despite the fact that the catalytic activity of tetrapyrazinoporphyrazine complexes, and the more so of tetraquinoxalinoporphyrazine complexes [8, 9], is higher than that of isometallic phthalocyanine complexes.

Therefore, in this study we examined the catalytic properties of recently prepared [14] metal complexes of network polytetrapyrazinoporphyrazine with continuous conjugation throughout the macromolecule, $(PzcM)_6$ (**Ia**–**Ic**), in a test reaction of hydrogen peroxide decomposition under heterogeneous conditions. An extremely important parameter in the heterogeneous catalysis is the catalyst particle size. Therefore, all samples of polymeric metal complexes were prepared under similar conditions, which ensured approximately equal values of the microcrystal size and active surface area.

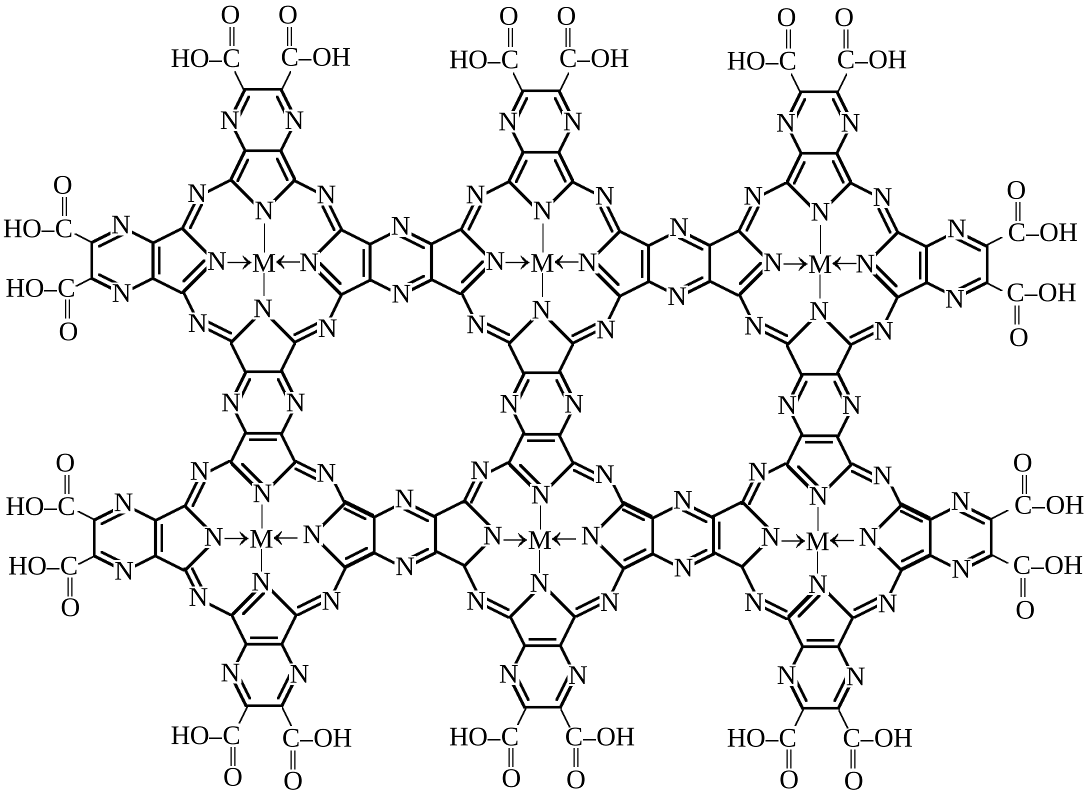
The decomposition of H_2O_2 in the presence of a catalyst is described by the equation

$$-dC_{H_2O_2}/d\tau = k_v C^m_{H_2O_2} C^n_{kat} \text{ or } -dC_{H_2O_2}/d\tau = k_{app} C^m_{H_2O_2},$$

where $k_{app} = k_v C^n_{kat}$; k_v is the true rate constant; $C_{H_2O_2}$, H_2O_2 concentration; C_{kat}, nominal molar concentration of monomeric units of the catalyst; n, reaction order

---

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



Ia–Ic

M = Cu (**a**), Co (**b**), Fe (**c**).

with respect to the catalyst; and *m*, reaction order with respect to the substrate.

The applicability of rate equations valid for homogeneous processes to the heterogeneous-catalytic reaction under consideration is due to the loose structure of the molecular lattice of the catalysts, permeable to substrate molecules and its decomposition products. Therefore, each monomeric unit of the polymer "operates," and fast diffusion processes do not control the rate of the catalytic reaction. On the other hand, approximately equal specific surface areas of all the catalysts studied provide approximately equal concentration of the active surface centers, proportional to the nominal catalyst concentration. This kinetic pattern was observed previously with metal complexes of monomeric tetra(heteroareno)porphyrazines [8, 9, 15, 16] and polyphthalocyanines [12, 13].

We studied the kinetics of hydrogen peroxide decomposition in the presence of $(PzcM)_6$ at $C^0_{H_2O_2}$ ~0.3 M and pH ~5. Experiments showed that all the metal complexes tested catalyze the decomposition of hydrogen peroxide and that the reaction is second-order with respect to the substrate under these conditions. As for the reaction order with respect to the catalyst, with $(PzcCu)_6$ it appeared to be fractional (1.59), which apparently suggests the participation of more than one monomeric unit in the elementary reaction event. The close fractional reaction order with respect to the catalyst (1.66) was found previously [12] for the decomposition of hydrogen peroxide in the presence of ruthenium polyphthalocyanine.

Assuming that the reaction order with respect to the catalyst is the same for all the metal complexes tested, we calculated from k_{app} and C_{kat} the true reaction rate constants (k_v), which can be used for comparing the catalytic activity of the compounds and calculating the activation energy of the process (see table).

The table shows that the catalytic activity of the polymeric metal complexes decreases in the order $(FePzc)_6 > (CoPzc)_6 > (CuPzc)_6$. This trend is consistent with that observed previously with complexes of the same metals with octaaza-substituted phthalo- and naphthalocyanines [9]. However, the activity increases in going from monomers to polymers. Whereas CuPzc exhibits no activity at all in the H_2O_2 decomposition, the calculated k_v^{293} in the presence of $(CuPzc)_6$ is 25 $l^{2.6}\,mol^{-2.6}\,min^{-1}$; the activity of CoPzc under

Kinetic parameters of H_2O_2 decomposition catalyzed by metal complexes of network polytetrapyrazinoporphyrazine

G_{kat}, mg	$[kat] \times 10^4$, (mol m.u.) l^{-1}	T, °C	k_{app}, l mol^{-1} min^{-1}	k_v, $l^{2.6}$ $mol^{-2.6}$ min^{-1}	$E^{\neq}$, kJ mol^{-1}
			$(CuPzc)_6(COOH)_{20}$		
9.9	15.57	40	0.0054 ± 0.0003	158	71 ± 5
10.1	15.86	60	0.032 ± 0.004	911	
5.0	7.85	70	0.0237 ± 0.0008	2085	
10.9	17.11	70	0.080 ± 0.004	2085	
15.0	23.55	70	0.137 ± 0.007	2085	
10.6	16.64	80	0.118 ± 0.008	3103	
			$(CoPzc)_6(COOH)_{20}$		
1.2	1.9	20	0.00265 ± 0.00002	2188	86 ± 5
1.2	1.9	40	0.029 ± 0.002	24191	
			$(FePzc)_6(COOH)_{20}$		
1.2	1.9	20	0.0144 ± 0.0006	11880	60 ± 3
1.2	1.9	40	0.0694 ± 0.0007	57298	
			$(CuPzc)_6(CN)_{20}$		
11.0	19.18	40	0.0094 ± 0.0006	196	36 ± 1
9.9	17.26	60	0.0194 ± 0.0009	479	
10.4	18.13	70	0.028 ± 0.002	651	

normal conditions increases in going to the hexamer by a factor of ~30, and that of FePzc, by a factor of more than 100. The activation energy increases by a factor of ~1.8 and ~1.2, respectively.

Comparison of the our data with those on the catalysis of H_2O_2 decomposition by metal polyphthalocyanine complexes shows that introduction of electron-withdrawing substituents into secondary conjugation contours of porphyrazine monomeric units enhances the catalyst activity. For example, at 40°C the activity of the ruthenium polyphthalocyanine complex, which is the most active among the related metal complexes [12], exceeds that of $(CuPzc)_6$ by only two orders of magnitude, is comparable with that of $(CoPzc)_6$, and is by a factor of more than 3 lower than that of $(FePzc)_6$.

Our studies also showed that variation of the initial H_2O_2 concentration in the range 0.07–0.33 M does not affect the catalyst activity.

To reveal the effect of terminal groups, we studied the catalytic properties of $(CuPzc)_6$ with carboxy and nitrile terminal groups. As seen from the table, the CN groups on the macromolecule periphery substantially decrease the activation energy of the process; as a result, the reaction rate constant grows with the temperature more slowly. This effect of the molecular periphery on the catalytic process in unexpected and difficult to explain.

EXPERIMENTAL

The catalytic properties of metal complexes were studied by the known method [6] using a temperature-controlled rocker. A reaction vessel was charged with 10 ml of ~1% H_2O_2 solution, after which an accurately weighed portion of a catalyst was added (the working catalyst concentration range was 0.7–2.2 mM monomeric units). The substrate consumption was monitored by the volume of the released oxygen. The initial H_2O_2 concentration was determined by iodometric titration.

Experiments were performed in the temperature range 298–353 K at initial pH ~5.

Metal complexes of network polytetrapyrazinoporphyrazine were prepared and purified by known methods [14] and identified by spectral characteristics and elemental analysis. Before use, samples of the catalysts were washed to neutral reactions of wash waters and absence of sulfates, dried to constant weight in a vacuum oven at 200°C and residual pressure of 2.7 kPa, and thoroughly ground.

To convert the terminal carboxy groups in copper polytetrapyrazinoporphyrazine into nitrile groups, the complex was treated with a threefold (relative to the terminal groups) excess of thionyl chloride for 5 h at 80°C. Then excess thionyl chgloride was removed, and the polymeric acid chloride formed was heated for 1 h at 60°C under reduced pressure (2.7 kPa), after which dry ammonia was admitted. The polymeric carboxamide thus obtained was suspended in anhydrous DMF and treated with a threefold (relative to the terminal groups) excess of thionyl chloride for 5 h at 80°C. The reaction product was isolated by filtration, washed on the filter with ice-cold water to neutral reaction and absence of Cl^- ions, dried, and identified by elemental analysis. Samples were pretreated before use as described above.

ACKNOWLEDGMENTS

The study was financially supported by the Russian Foundation for Basic Research (project no. 03-03-96472).

REFERENCES

1. Korzhenevskii, A.B., Markova, L.V., Efimova, S.V., Koifman, O.I., and Zelenov, A.A., *Zh. Obshch. Khim.*, 2005, vol. 75, no. 6, p. 1041.
2. Cook, A.H., *J. Chem. Soc.*, 1938, vol. 60, p. 1761.
3. Sittig, M., *Oxo Processes and Products*, Park Ridge, New Jersey: Noyes Development, 1966.
4. Mazgarov, A.M. and Vil'dakov, A.F., Abstracts of Papers, *XVIII Mendeleevskii s"ezd po obshchei i prikladnoi khimii* (XVIII Mendeleev Congr. on General and Applied Chemistry), Kazan, 2003, vol. 4, p. 331.
5. Yu Cai Cao and Xuan Zhen Jiang, *J. Mol. Catal. A: Chem.*, 2002, vol. 184, nos. 1–2, p. 183.
6. Borisenkova, S.A., Il'ina, L.M., Leonova, E.V., and Rudenko, A.P., *Zh. Org. Khim.*, 1973, vol. 9, no. 9, p. 1827.
7. Borisenkova, S.A., Erokhin, A.S., Novikov, V.A., and Rudenko, A.P., *Zh. Org. Khim.*, 1975, vol. 11, no. 9, p. 1977.
8. Maizlish, V.E., Korzhenevskii, A.B., and Klyuev, V.N., *Khim. Geterotsikl. Soedin.*, 1984, no. 9, p. 1257.
9. Korzhenevskii, A.B., Shikova, T.G., Bykova, V.V., and Koifman, O.I., *Zh. Obshch. Khim.*, 2002, vol. 72, no. 7, p. 1202.
10. Roginskii, S.E., Berlin, A.A., Golovina, O.A., Dokukina, E.S., Sakharov, M.M., and Cherkashina, L.G., *Kinet. Katal.*, 1963, vol. 4, no. 3, p. 431.
11. Berezin, B.D. and Shlyapova, A.N., *Izv. Vyssh. Uchebn. Zaved., Ser. Khim. Khim. Tekhnol.*, 1969, vol. 12, no. 12, p. 1641.
12. Shlyapova, A.N. and Berezin, B.D., *Izv. Vyssh. Uchebn. Zaved., Ser. Khim. Khim. Tekhnol.*, 1971, vol. 14, no. 12, p. 1810.
13. Shlyapova, A.N. and Berezin, B.D., *Tr. Ivanov. Khim.-Tekhnol. Inst.*, 1973, no. 15, p. 89.
14. Korzhenevskii, A.B., Markova, L.V., Efimova, S.V., Koifman, O.I., and Krylova, E.V., *Zh. Obshch. Khim.*, 2005, vol. 75, no. 6, p. 1036.
15. Pobedinskii, S.N., Trofimenko, A.A., and Zharnikova, M.A., *Izv. Vyssh. Uchebn. Zaved., Ser. Khim. Khim. Tekhnol.*, 1985, vol. 28, no. 12, p. 46.
16. Kreja, L., *Monatsh. Chem.*, 1987, vol. 118, nos. 6–7, p. 717.