METAL COMPLEXES OF TETRAPYRAZINOPORPHYRAZINES — EFFECTIVE CATALYSTS OF THE OXIDATION OF MERCAPTANS

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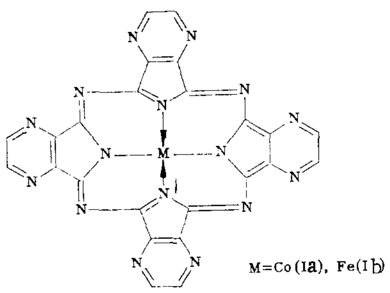
The catalytic activity of the tetrapyrazinoporphyrazine complexes of cobalt and iron have been studied in the oxidation of aliphatic mercaptans by molecular oxygen. n-Butyl mercaptan was used as the model compound. The metallotetrapyrazinoporphyrazines tested exhibited a considerably higher catalytic activity than cobalt phthalocyanine.

The high catalytic activities of the phthalocyanines of the transition metals and other similar structures in a number of redox reactions has been the object of numerous investigations [1, 2]. In recent years, these compounds have found wide use as catalysts for the industrial purification of petroleum products from mercaptans [1-4]. The greatest catalytic activity in these processes is exhibited by cobalt phthalocyanine and its derivatives [5-7].

Some authors [8] connect the catalytic activity of such complex compounds wholly with the nature of the complex-forming metal. However, it has recently been shown [7, 9-11] that the activity of the complexes is affected not only by the nature of the complex-forming metal but also by the structure of the macroheterocyclic ligand. Thus, for example, when the benzene rings of the metallophthalocyanines are replaced by dithiacyclohexene rings, the catalytic activity of the resulting complexes in the oxidation of the thiols falls somewhat [7, 10]. And when the benzene rings are replaced by pyridine rings, i.e., when metallotetrapyridinoporphyrazines are used as catalysts, it increases [11].

In order to expand our ideas on the influence of the nature of the macro ring on the above-mentioned process, we have studied the catalytic activity of metallocomplexes with a different structure of the organic ligand — metallotetrapyrazinoporphyrazines — in the oxidation of mercaptans. We have shown that the Co and Fe complexes of tetrapyrazinoporphyrazin (Ia, Ib) are far more effective catalysts of the oxidation of mercaptans than the Co complex of phthalocyanine (II). Thus, after 15 min the degree of oxidation of sodium n-butyl mercaptide in the presence of the catalysts (Ib) and (Ia) reached 92% and 98% (by weight), respectively, and in the presence of catalyst (II) it was only 5%.

It can be seen from the facts given that the structure of the macroheterocyclic ligand exerts a considerable influence on the catalytic properties of metal complexes with the porphyrazine structure in the oxidation of thiols. In view of this it is impossible to agree with Simonov et al. [8], who connect the catalytic activity of some catalysts wholly with the nature of the metal. It would be more correct, in our opinion, to apply to these com-



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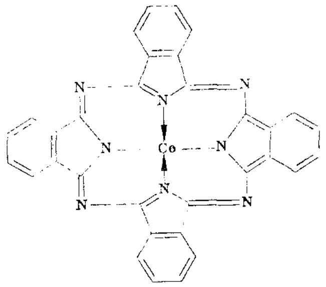

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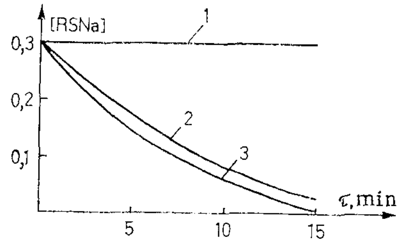

Fig. 1. Kinetic curves of the oxidation of sodium n-butyl mercaptide by molecular oxygen in the presence of catalysts: 1) cobalt phthalocyanine; 2) iron tetrapyrazinoporphyrazine; 3) cobalt tetrapyrazinoporphyrazine.

pounds the idea of molecular catalysis [12], i.e., to consider the whole assembly of elements of the molecule as important component parts of the catalyst, each of them playing a specific role in the complex catalytic process.

The catalytic activity of metallophthalocyanines is apparently connected with their capacity for forming an oxygen adduct and a ternary oxygen—catalyst—substrate complex [13]. Consequently, a considerable increase in the catalytic activity of complexes of the phthalocyanine structure when the benzene rings are replaced by pyrazine rings causes no surprise, since this leads to a change in the geometric parameters and the electronic structure of the molecule of the complex. Furthermore, in the metallotetrapyrazinoporphyrazines there is an easier migration of electrons than in the metallophthalocyanines because of the free electron pairs of the nitrogen atoms of the pyrazine rings and, obviously, the oxidation and reduction reactions of the complex take place more intensively [11].

Thus, among the factors responsible for the increased catalytic activity of phthalocyanine compounds in the oxidation of mercaptans one must include a rise in the electron-accepting capacity of the ligand and the localization of a partial positive charge on the metal atom and a negative charge on the organic moiety of the molecule.

EXPERIMENTAL

The complexes studied were obtained by a known method [14] and were tested as catalysts in the oxidation of aliphatic mercaptans with molecular oxygen. n-Butyl mercaptan was chosen as the model substance.

The catalytic oxidation of this thiol with molecular oxygen to the corresponding disulfide was carried out at atmospheric pressure in a 10% aqueous solution of caustic soda in a batch apparatus [7]. The trial was performed in the laboratory of VNIIUS [All-Union Scientific-Research Institute of Hydrocarbon Raw Material] (Kazan').

The reactor — a cylindrical glass vessel with a capacity of 500 ml fitted with a turbine stirrer, a bubbler, a sampling device, a reflux condenser, and baffle plates — was charged with a solution of n-butyl mercaptan in 10% aqueous caustic soda (the concentration of mercaptan sulfur was 0.3 M). The stirrer was switched on and the reaction mixture was thermostated at 30°C. After the temperature conditions had become established and a speed of rotation of the stirrer of 200 rpm had been reached, 0.02% (by weight) of the catalyst was added. Oxidation was carried out with molecular oxygen, which was bubbled into the reaction mixture (a rate of flow of the oxygen of 300 ml/min).

Samples were taken during the experiment and the concentrations of mercaptide in the reaction mixture were determined by the potentiometric titration of the mercaptide with silver ammoniate on a pH-340 instrument.

The kinetic curves of the oxidation of sodium n-butyl mercaptide with molecular oxygen in the presence of cobalt and iron tetrapyrazinoporphyrazines and cobalt phthalocyanine are given in Fig. 1.

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kine-SUBSTITUTION IN THE N-[ω-(5-BROMOURACIL-1-YL)ALKYL]ALKYLAMINE SERIES

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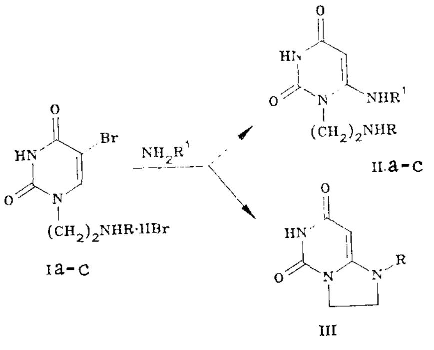
In the reaction of N-[2-(5-bromouracil-1-yl)ethyl]alkylamines with alkylamines at 40°C kine-substitution takes place with the formation of N-[2-(6-alkylamino-uracil-1-yl)ethyl]alkylamines.

As we have reported, the reaction of N-[ω-(5-bromouracil-1-yl)alkyl]alkylamines (Ia-c) with amines of different nucleophilicities (propylamine, butylamine, morpholine) at the boiling point of the reaction mixture takes place with the formation of bicyclic systems [1, 2]. The aim of the present investigation was to study the influence of the temperature on the course of the reaction. After mixtures of compound (Ia) with propylamine and butylamine and of (Ib) with butylamine had been kept at 40°C for 2 h, the main reaction products isolated were the N-[2-(6-alkylaminouracil-1-yl)ethyl]alkylamines (IIa-c), respectively.



I a) $R=C_3H_7$; b) $R=C_4H_9$; c) $R=CH_2C_6H_5$;
II a) $R=R^1=C_3H_7$; b) $R=C_3H_7$, $R^1=C_4H_9$;
c) $R=R^1=C_4H_9$

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