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Effect of the Structure of the Macroheterocyclic Ligand on the Catalytic Properties of Tetraarenoporphyrazine Metal Complexes: II.[1] Oxidation of Cysteine, Catalyzed by Cobalt Tetraarenoporphyrazines

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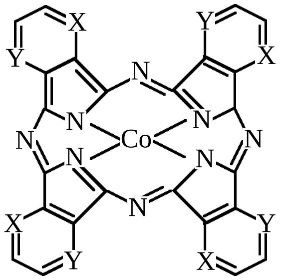
Abstract—The catalytic activity of cobalt tetraarenoporphyrazine complexes in heterogeneous oxidation of cysteine is much dependent on the macrocycle structure and is inversely related to the electron-acceptor power of the ligand.

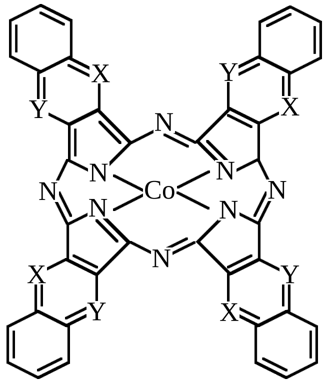
At present both water-soluble [2, 3] and insoluble [4] transition metal phthalocyanine complexes have been studied as catalysts in oxidation of sulfur-containing compounds, such as hydrogen sulfide, ethanethiol, and cysteine.

Cystein oxidation with molecular oxygen is widely used as a model for the industrially important oxidation of thiols into disulfides. The reaction is activated by various metal phthalocyanine complexes. The most active is PcCo, its activity in heterogeneous conditions being two orders of magnitude lower than in homogeneous, iron phthalocyanine, too, is active both in heterogeneous and homogeneous conditions [4], whereas copper phthalocyanine exhibits low activity in homogeneous conditions and is absolutely inactive is heterogeneous [5].

To assess the effect of the nature of the macrocyclic ligand on the catalytic properties of cobalt tetraarenoporphyrazines in cysteine oxidation, we compared the catalytic activity of cobalt complexes of tetra-2,3-pyridinoporphyrazine (2,3-PycCo) (**Ib**), tetrapyrazinoporphyrazine (PzcCo) (**Ic**), 2,3-naphthalianine (2,3-NcCo) (**IIa**), tetra-2,3-quinolinoporphyrazine (2,3-QlcCo) (**IIb**), and tetra-2,3-quinoxalinoporphyrazine (2,3-QxcCo) (**IIc**) with that of cobalt phthalocyanine (PcCo) (**Ia**).



Ia–Ic



IIa–IIc

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

There are several concepts of the mechanism of catalytic oxidation of thiols in the presence of metal complexes, based on the hypothesis of changing transition metal valence [6].

The kinetics and mechanisms of heterogeneous oxidation of thiols in the presence of metal phthalocyanines have been studied in [7–9]. Borisenkova [7]

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

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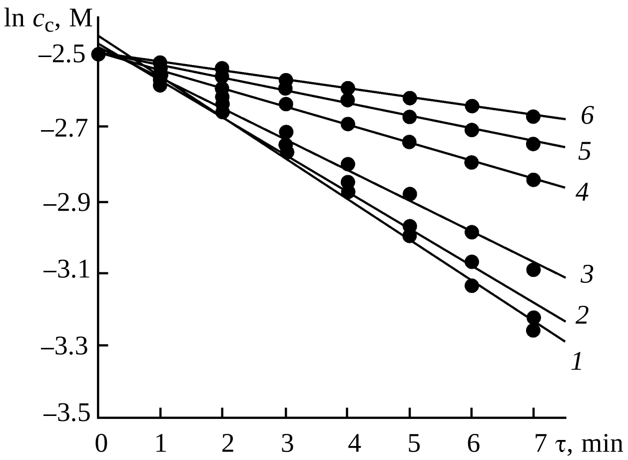

Fig. 1. Kinetic curves for cysteine oxidation at 298 K in the presence of cobalt arenoporphyrazines (*c*, M): (*1*) 2,3-NcCo (1.98), (*2*) PcCo (1.75), (*3*) 2,3-QlcCo (2.4), (*4*) 2,3-PycCo (1.73), (*5*) 2,3-QxcCo (3.01), and (*6*) PzcCo (5.46).

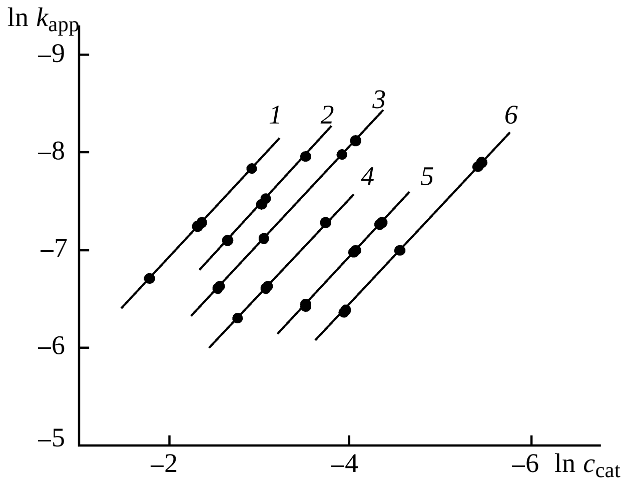

Fig. 2. Plot of ln k_{app} vs. ln c_{cat} for cysteine oxidation at 298 K in the presence of (*1*) PzcCo, (*2*) 2,3-QxcCo, (*3*) 2,3-PycCo, (*4*) 2,3-QlcCo, (*5*) PcCo, and (*6*) 2,3-NcCo.

found that cystein is only oxidized in alkaline media where its thiolic group is deprotonated; the reaction begins with coordination of the substrate anion with the metal ion; the reaction rate depends on the pH of the solution and directly related to the partial pressure of oxygen in the system, and the rate-limiting stage is reaction between O_2 and the adduct of the catalyst with the thiol anion ($Ct \cdot RS^-$).

According to general concepts of chemical kinetics and published data, we can write the following equation for the cystein oxidation rate.

$$-dc_c/d\tau = k_t – c_t^m – c_{cat}^n – c_{O_2}^p \quad \text{or} \quad -dc_t/d\tau = k_{app} – c_c^m.$$

Here $k_{app} = k_t – c_{cat}^n – c_{O_2}^p$, c_c is the cysteine concentration, c_{cat} is the arbitrary molar catalyst concentration [1], $c_{O_2}^p$ is the oxygen concentration, k_t and k_{app} are the true and apparent reaction rate constants, and *m*, *n*, and *p* are the reaction orders in the corresponding component.

By the Winkler method we found that the initial concentration of oxygen in the reaction medium is 1.05×10^{-3} M.

Taking into account that the gas phase over the reaction mixture always consisted of oxygen and the pressure in the system was maintained equal to atmospheric thus ensuring effective transfer of oxygen from the gas phase into water, we can consider the oxygen concentration during experiment constant.

Based on earlier data for PcCo-catalyzed cysteine oxidation, we chose experimental conditions providing the highest reaction rate (1% solution of cysteine in 2% sodium hydroxide, pH 12.35).

It was found that in the presence of all the metal complexes studied the process is first-order in substrate (Fig. 1). From the kinetic curves we calculated apparent reaction rate constants (k_{app}) and estimated reaction order by the arbitrary molar catalyst concentration (c_{cat}) (Fig. 2). The reaction order was equal to one in all the cases.

In view of the fact that the reaction orders in the presence of PcCo and the other metal complexes are the same both in substrate and catalyst, we proposed a common reaction mechanism with all the cobalt tetraarenoporphyrazines (Figs. 1 and 2).

The k_t value found from k_{app}, c_{cat}, and c_{O_2} (the reaction order in oxygen was taken to be one), can be used for comparing the catalytic activities of the compounds and for calculating the activation energy and entropy of the reaction studied.

The table lists the experimental and calculated kinetic parameters. As seen, the reaction rate decreases in the order 2,3-NcCo > PcCo > 2,3-QlcCo > 2,3-PycCo > 2,3-QxcCo > PzsCo.

The activation parameters reveal a compensation effect for all the cobalt tetraarenoporphyrazines studied (Fig. 3). This result provides evidence for our assumption of a common mechanism with all the macroheterocycles. Consequently, the mechanism proposed for the catalytic oxidation of cysteine on PcCo is also valid for the reactions that occur on the other complexes studied.

Catalytic activity of cobal complexes of phthalocyanine and its structural analogs in cysteine oxidation[a]

T, K	$c_{cat} \times 10^2$, M	$k_{app} \times 10^4$, s^{-1}	k_t, $l\ s^{-1}\ mol^{-1}$	$c_{cat} \times 10^2$, M	$k_{app} \times 10^4$, s^{-1}	k_t, $l\ s^{-1}\ mol^{-1}$
		PcCo			2,3-PycCo	
298	1.29	6.83±0.18	50.51	1.73	2.94±0.12	16.23
	1.75	9.24±0.48	50.53	4.76	8.11±0.31	16.23
	3.04	16.13±1.02	50.53	7.86	13.40±1.03	16.23
303	0.59	3.81±0.15	61.60	1.89	4.07±0.11	20.55
	1.12	7.23±0.23	61.59	4.79	10.33±0.50	20.55
	1.80	11.65±0.63	61.60	9.70	20.94±2.28	20.55
313	0.66	6.24±0.22	89.72	2.06	6.96±0.14	32.23
	1.14	10.77±0.53	89.74	3.78	12.80±0.93	32.24
	2.31	21.76±2.08	89.74	6.77	22.91±2.58	32.24
$E^{\neq}$, kJ/mol/$\Delta S^{\neq}$, J K^{-1} mol^{-1}		29.7/–121			35.5/–111	
		PzcCo			2,3-NcCo	
298	5.46	3.96±0.16	6.90	0.45	3.87±0.21	82.59
	9.86	7.15±0.46	6.90	1.05	9.14±0.57	82.59
	16.99	12.32±0.86	6.90	1.98	17.17±1.18	82.58
303	9.83	9.29±0.39	9.01	0.49	5.07±0.19	98.79
	12.62	11.94±0.67	9.01	1.01	10.46±0.38	98.87
	19.61	18.55±1.61	9.01	1.76	18.27±1.37	98.83
313	3.85	6.05±0.16	14.97	0.51	7.50±0.25	139.14
	7.50	11.78±0.51	14.97	1.04	15.23±1.07	139.24
	14.91	23.44±2.69	14.97	1.45	21.26±2.20	139.24
$E^{\neq}$, kJ/mol/$\Delta S^{\neq}$, J K^{-1} mol^{-1}		40.0/–103			27.0/–126	
		2,3-QlcCo			2,3-QxcCo	
298	2.40	6.93±0.38	27.53	3.01	3.50±0.05	11.08
	4.63	13.37±0.88	27.53	4.89	5.69±0.25	11.08
	6.40	18.50±1.59	27.53	7.12	8.28±0.18	11.08
303	2.57	9.25±0.59	34.29	2.62	3.91±0.17	14.22
	3.32	11.97±0.64	34.29	5.30	7.92±0.34	14.22
	5.47	19.69±1.57	34.29	9.54	14.25±0.97	14.22
313	0.71	3.88±0.16	52.10	1.18	2.83±0.2	22.88
	1.33	7.27±0.41	52.09	2.67	6.43±0.2	22.89
	2.93	16.02±2.19	52.11	7.88	18.95±0.2	22.89
$E^{\neq}$, kJ/mol/$\Delta S^{\neq}$, J K^{-1} mol^{-1}		33.0/–115			37.5/–107	

[a] The errors in $E^{\neq}$ (kJ/mol) and $\Delta S^{\neq}$ (J K^{-1} mol^{-1}) are 10%.

Our results show that, like in the catalytic decomposition of hydrogen peroxide [1], the structure of the macroheterocyclic ligand exerts a considerable effect on the catalytic activity of metal complexes. Thus, peripheral aza substitution reduces the catalytic activity, whereas benzannelation both of phthalocyanine and of its aza analogs enhances it.

At first glance, such a relationship between the structure of the ligand and its catalytic activity may seem unexpected, especially in view of the earlier established fact that metal phthalocyanines are less active catalysts than tetrapyrazinoporphyrazine complexes [10].

On the other hand, our data are supportive of the mechanism proposed in [7] for oxidation of thiols with molecular oxygen and involving reaction of $Cat \cdot RS^-$ with O_2 as a limiting stage. The latter reaction is favored by increased partial negative charge on the metal atom [11].

Actually, provided this mechanism is operative, the least active should be the complex of a phthalocyanine octaaza substituted in the periphery, tetrapyrazinoporphyrazine, containing eight strongly elec-

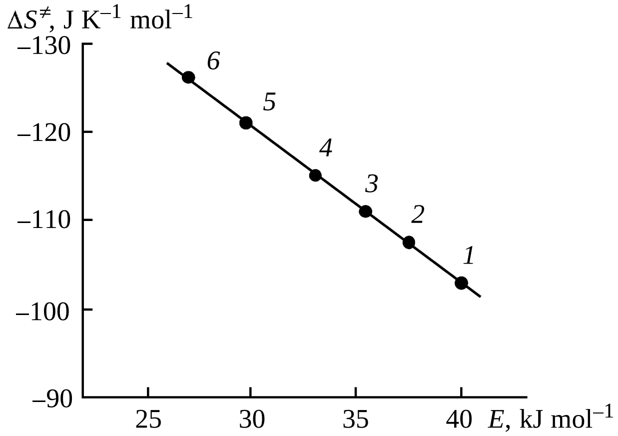

Fig. 3. Compensation effect in cystein oxidation in the presence of (*1*) PzsCo, (*2*) 2,3-QxcCo, (*3*) 2,3-PysCo, (*4*) 2,3-QlcCo, (*5*) PcCo, and (*6*) 2,3-NcCo.

tron-acceptor aza groups in the 3 and 4 positions of benzene rings. The electronic effect of octaaza substitution can be assessed on the basis of the hypsochromic shift of the first band in the electronic absorption spectrum in going from PcCo to PzsCo ($\Delta\lambda_1$ 147 nm in sulfuric acid).

Linear benzannelation, by contrast, considerably increases the electron density on the major choromophore, i.e. can be considered as electron-donor substitution in the periphery of phthalocyanine, which is clearly seen from a considerable bathochromic shift of the *Q* band in the electronic absortion spectrum in going from PcCo to 2,3-NcCo ($\Delta\lambda_1$ 75 nm in sulfuric acid).

Thus, the catalytic activity of cobalt complexes of phthalocyanine and its aza analogs is enhanced by benzannelation. Therewith, this effect is not strong sufficiently to compensate for the adverse effect on the catalytic activity of four aza atoms, as judged from the fact that 2,3-QxcCo stands after 2,3-PycCo in the activity order, while 2,3-QlcCo stands after PcCo.

EXPERIMENTAL

The catalytic properties of metal complexes were studied by the procedures in [7] using a temperature-controlled rocker. Substrate concentration was followed by the volume of absorbed oxygen.

Experiments were performed at 298–313 K.

Metal tetraarenoporphyrazines were prepared and purified as described in [12–14] and identified by spectral characteristics [12–14]. Catalysts were treated with water to neutral and sulfate-free washings, dried to constant weight at 423 K, and thoroughly ground before use.

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