AUTOOXIDATION OF HYDRAZINE CATALYZED BY TETRASULPHOPHTHALOCYANINES

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The effect of Co(II), Cu(II), Ni(II), Mn(III), and Fe(III) tetrasulphophthalocyanines on the auto-oxidation of hydrazine has been studied but only the cobalt complex has been found to possess a distinct catalytic effect. Differences in catalytic activity are explained by different ability of the complex to bind reversibly molecular oxygen. The kinetics of the autooxidation catalyzed by cobalt tetrasulphophthalocyanine can be described by the Michaelis-Menten law. Ternary complex $[N_2H_4.\text{cobalt tetrasulphophthalocyanine}.O_2]$ is an active intermediate of the reaction.

The reactions of molecular oxygen with multiequivalent substrates are likely enabled by the presence of metal ions as catalysts[1]. An attempt has been made in this paper to study catalytic effects of metal ions bound in stable chelates. In this way, side reactions of free cations as interaction with solvent, formation of basic condensed ions *etc.*, are cut down. The use of tetravalent ring chelates seems to be of advantage because of their high stability and the invariant structure. Metal chelates of this kind are often oxygen carriers[2] and active centres of biocatalysts[3]. In this paper, tetrasulphophthalocyanines of some transition metals (*I*) have been used which in structure and properties are similar to porphyrins; however, they are readily soluble in water and can be easily prepared. In order to study their catalytic effect, the reaction of molecular oxygen with hydrazine has been selected, as it is a simple complementary reaction with only one reaction product — molecular nitrogen.

EXPERIMENTAL

Reagents. Complexes of 4, 4′, 4″, 4‴-phthalocyanine tetrasulphonic acid (*I*) with Co(II), Cu(II), Ni(II), Fe(III) and Mn(III) were prepared[4] by melting sodium 4-sulphophthalate, urea, ammonium chloride, and chloride of the appropriate metal at the temperature of 160—180°C. The crude product was purified by repeated dissolving and salting out from aqueous solution; the entrained salts were removed from the product by washing with 80% ethanol and subsequent extraction with absolute ethanol. Other reagents used were of R. G. purity; hydrazine dihydrochloride was repurified by crystallization from aqueous solution.

The absorption spectra of the solutions of tetrasulphophthalocyanine complexes were established using recording spectrophotometer Unicam SP 800 B. The absorption spectra of tetrasulphophthalocyanine complexes were followed during the reaction directly in the photometer

cell sealed with a silicon rubber cap. A hypodermic syringe punctured in the rubber closure was used to introduce nitrogen into the cell. Nitrogen was freed from oxygen traces by passing through wash bottles with chromium dichloride solution and alkaline hydrazine solution with cobalt tetrasulphophthalocyanine. The same procedure was made use of when proving the existence and composition of the *I*-Co complex with hydrazine by the continuous variation method. The method was employed for equimolar and nonequimolar solutions of the components, the extinction was measured at the wave-length of 450 nm.

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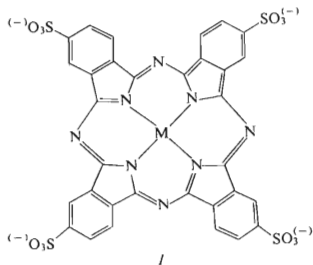
The kinetics of the autooxidation of hydrazine was examined in test-tubes dipped in the thermostat (25°C). The test-tubes were fitted with a ground stopper with gas inlet tube. Prior to the reaction hydrazine dihydrochloride solution was thoroughly bubbled through with nitrogen; the reaction was initiated by injection of the catalyst solution, the oxygen inlet being opened at the same time. The oxygen flow rate was kept constant and high enough (450 ml/min) so that the reaction rate was not limited by diffusion of oxygen. The constant oxygen concentration given by partial pressure of oxygen $p_{O_2} = 760$ Torr was $1.23 \cdot 10^{-3}$M. The reaction was stopped by acidifying the solution with concentrated hydrochloric acid. Hydrazine was determined by bromate titration with potentiometric indication. Titrimeter TTT 1c (Radiometer-Denmark) was employed for pH measurements and potentiometric titration.

RESULTS AND DISCUSSION

Catalytic Effect of Tetrasulphophthalocyanine Complexes

Catalytic effect of tetrasulphophthalocyanine is remarkably dependent on the nature of the central ion[5] (Table I). Whereas addition of cobalt tetrasulphophthalocyanine (CoTSP) in concentration of $1 \cdot 10^{-5}$M causes almost immediate oxidation of all the hydrazine, addition of any of the other complexes in the same concentration brings about only a low effect. The autooxidation of hydrazine in solution without the addition of tetrasulphophthalocyanine is obviously caused by catalytic effect of trace impurities. According to Audrieth and Mohr[6] the noncatalyzed reaction proceeds at immeasurably slow rate. The low catalytic effect of iron(III)-, manganese(III)-, copper(II)-, and nickel(II)tetrasulphophthalocyanines is likely due to the content of free cations in the substances. Weber and Busch[4] drew attention to the

TABLE I

Catalytic Effect of Tetrasulphophthalocyanine Complexes on Autooxidation of Hydrazine

Initial concentration $5 . 10^{-2}$M-N_2H_4.2 HCl; 0·5M-NaOH. Catalyst concentration in all cases $1 . 10^{-5}$ mol/1 s, only for CoTSP — $1 . 10^{-7}$ mol/ 1 s.

Catalyst	Conversion of N_2H_4, % after 10 min	Turn-over number[a]	Catalyst	Conversion of N_2H_4, % after 10 min	Turn-over number[a]
—	6·0	—	NiTSP	14·7	70
FeTSP	10·3	49	MnTSP	17·5	83
CuTSP	10·9	52	CoTSP	44·8	22 000

[a] Number of hydrazine molecules brought to reaction by one molecule of the complex within 1 min

metal impurities in the given complexes and to the difficulty connected with a complete purification of the substance.

The differences in catalytic properties of tetrasulphophthalocyanine complexes are associated with changes in the absorption spectra of the system N_2H_4–O_2–CoTSP. The absorption spectrum of CoTSP in alkaline solution has two maxima at 626 and 670 nm, the former belonging to the cobalt complex, the latter to the adduct of CoTSP with molecular oxygen[7]. By addition of hydrazine, the original maxima disappear and maxima at 450 and 680 nm arise; the latter may be a branch of the original maximum at 670 nm. After bubbling with oxygen hydrazine disappears from the
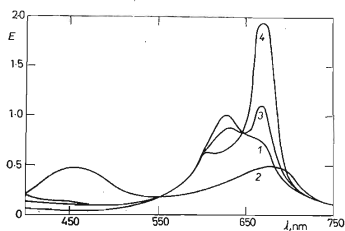

FIG. 1

Changes in Absorption Spectrum of CoTSP, due to Hydrazine and Oxygen $2 . 10^{-5}$M-CoTSP; $1 . 10^{-2}$M-N_2H_4; 0·5M-NaOH

1 Fresh CoTSP solution; 2 on addition of hydrazine; 3 on bubling O_2 through — 15 min; 4 on bubbling O_2 through — 30 min.
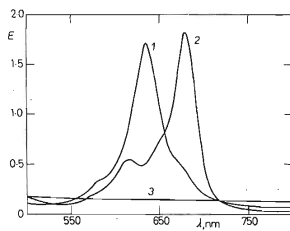

FIG. 2

Changes in Absorption Spectra of FeTSP, due to Hydrazine and Oxygen $3 . 10^{-5}$M-FeTSP; $1·5 . 10^{-2}$M-N_2H_4; 0·1M-NaOH

1 Fresh FeTSP solution; 2 on addition of hydrazine; 3 on bubbling O_2 through.

solution and the original absorption spectrum (maxima at 626 and 670 nm) returns, but the relative heights of the maxima are changed (Fig. 1). Catalytic properties of the solution remain unchanged so that the cycle of changes raised by addition of hydrazine and subsequent bubbling with oxygen can be repeated many times. The original absorption spectrum is produced likewise after acidifying the solution containing hydrazine, even if it is made under strictly anaerobic conditions.

The addition of hydrazine to alkaline solution of FeTSP and MnTSP causes also a distinct change in the absorption spectrum. In the FeTSP solution, the maximum at 634 nm, which is assigned[8] to both Fe(III)TSP and the adduct of Fe(II)TSP with oxygen, disappears and a new one appears at 680 nm (Fig. 2). The spectra of MnTSP solutions and their changes are more complicated. In both cases, however, the subsequent bubbling with oxygen causes rapid decolourizing of the solution, apparently due to oxidative degradation of the ligand. In absence of hydrazine both complexes are considerably more stable towards oxygen. The absorption curves of CuTSP and NiTSP exhibit no changes after addition of hydrazine and bubbling with oxygen; they neither change with time.

The catalytic activity of tetrasulphophthalocyanine complexes is obviously connected with the ability of the central atom to bind extraplanar ligands, *i.e.* to occupy coordination sites on the axis perpendicular to the ligand plane. Owing to a strong ligand field of the tetrasulphophthalocyanine anion, copper and nickel tetrasulphophthalocyanines have minimum tendency to bind further ligands to form octahedral complexes. Therefore, they turned out as nonreactive to hydrazine and oxygen and hence inactive as catalysts.

MnTSP in the solution is subject to hydrolytic changes[9] in absence of hydrazine, however, no interaction with oxygen was observed. On the other hand, existence of an oxygen adduct of ferrous complex with oxygen $(FeTSP)_2O_2$ is known, the complex being stable in neutral medium; in alkaline solution it is decomposed irreversibly[7]. The influence of hydrazine on the spectra of both complexes can be caused either by reduction of the complex[10,11], or by coordination of hydrazine as extraplanar ligand. Of course, a mere reduction of the central atom does not account for the rapid decomposition of the complex in presence of oxygen. Consequently, a deeper intervention into structure of the whole complex, perhaps formation of unstable intermediate with hydrazine and oxygen, must be involved.

From the complexes under investigation the CoTSP only forms in alkaline solution a stable, reversible adduct with molecular oxygen[7]. It exhibits, as the only one, strong catalytic effect on the autooxidation of hydrazine. For that reason, further attention was paid to its catalytic properties and effect of some other nucleophilic substrates on the absorption spectrum of CoTSP in presence or absence of oxygen was studied. The same behaviour was observed in presence of hydroxylamine, ascorbic acid, sulphide, and arsenite. With the latter two, however, the change in the spectrum is less distinct and not completely reversible. Further substrates as ferrocyanide,

cyanide, thiocyanate, sulphite, and thiosulphate do not change the spectrum, but they accelerate increase of the maximum at 670 nm belonging to the adduct of CoTSP with oxygen.

The absorption maximum at 450 nm produced by reaction of hydrazine with CoTSP was observed also by other authors and assigned on the basis of the decrease of magnetic moment to the reduction of Co(II)TSP to Co(I)TSP[10,11]. The maximum at the same wave-length, appears also as a result of the interaction of CoTSP with substrates which cannot be assumed to be able to reduce bivalent cobalt. A comparison of standard potentials[12] of the substrates in alkaline medium shows that there is no direct connection between the standard potential and formation of the maximum at 450 nm. For example, addition of sulphite having redox potential E_B^0 0·93V does not produce a maximum, whereas arsenite (E_B^0 0·67 V) and sulphite (E_B^0 0·48 V) do.

This change in the spectrum may likewise be due to the entering of the substrate into the coordination sphere of the tetrasulphophthalocyanine complex. The continuous variation method proved the existence of an 1 : 1 complex of CoTSP with hydrazine. Stability constant of this complex, determined from the Job curve[13], amounts to $7·8 . 10^5$. Provided that hydrazine would reduce the cobalt complex, the dependence of extinction upon the composition of the solution, measured at 450 nm, could not pass through the maximum. In that case only a break at the ratio CoTSP : N_2H_4 = = 4 : 1 which corresponds to stoichiometry of the reduction could occur.
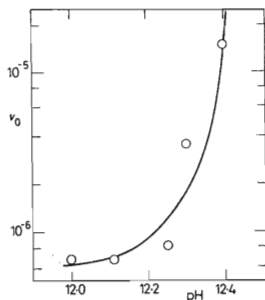

FIG. 3

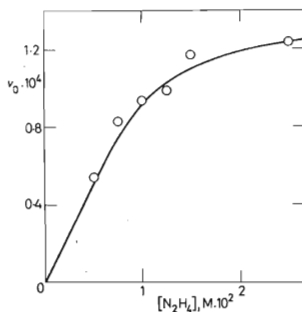Plot of v_0 against Initial Concentration of Hydrazine
$1 . 10^{-6}$M-CoTSP; 1M-NaOH.

FIG. 4

Plot of v_0 against pH
$1 . 10^{-6}$M-CoTSP; $1 . 10^{-2}$M-N_2H_4.

Kinetics of Catalyzed Autooxidation of Hydrazine

Catalyzed autooxidation of hydrazine using CoTSP as catalyst proceeds at pH > 12 only. Therefore 0.5M-NaOH, in some cases also 1M-NaOH, was used as reaction medium. Since the plots of actual hydrazine concentration against time do not correspond to a simple reaction order, the method of initial rates was employed to describe kinetics of the reaction. The initial reaction rate v_0 was determined from these curves as tangent in the origin. A plot of v_0 against initial hydrazine concentration (Fig. 3) shows that the course of the reaction corresponds to a transition between first and zero order kinetics. This dependence can be described by the Michaelis–Menten relationship often used in enzyme kinetics[5]. For the initial reaction rate it holds that

$$v_0 = kK[P]_0 [S]/(1 + K[S]), \qquad (1)$$

where k is the rate constant, K the equilibrium constant whose exact meaning depends on the reaction mechanism, $[P]_0$ the concentration of catalyst, and $[S]$ denotes the concentration of substrate N_2H_4. The limiting rate at high substrate concentration is equal to $k[P_0]$, from which the constant k can be calculated. K is determined under condition that for $v_0 = kP_0/2$, $[S] = 1/K$.

Validity of the relationship was verified by two graphical methods. Linearization of equation (1) to the form

$$1/v_0 = 1/k[P]_0 + (1/kK[P]_0) \cdot (1/[S]), \qquad (2)$$

makes it possible to determine constants k and K by plotting $1/v_0$ against $1/S$. The second procedure started from relation

$$v_0/[S] = kK[P]_0 - Kv_0. \qquad (3)$$

Values of the constants are obtained by plotting $v_0/[S]$ against v_0.

Table II presents a list of the found values of constants, determined by the procedures mentioned.

The dependence of v_0 on pH is unusually steep (Fig. 4) and could be experimentally followed within 0.4 of the pH unit only. The buffered medium of pH > 12.4 can hardly be realized, at pH < 12.0 the reaction does not proceed. In unbuffered solutions of 0.1 − 1.0M-NaOH it was found that initial reaction rate was independent of the concentration of hydroxyl ions.

The dependence of v_0 on the concentration of CoTSP was followed within $5 \cdot 10^{-8}$ to $1 \cdot 10^{-5}$M. The initial rate v_0 increased at first linearly with the concentration, at higher concentrations $5 \cdot 10^{-6}$M a curvature towards lower values appeared. Deflection from linearity diminished with the increasing flow rate of oxygen. Hence it follows that the reaction rate at higher catalyst concentration is limited by the oxygen diffusion.
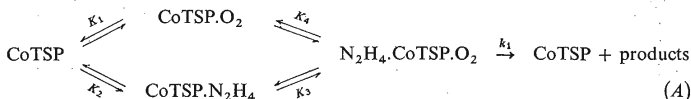
TABLE II
Constants k and K, Determined by Various Graphical Methods

	1M-NaOH		0·5M-NaOH		Graph coordinates	
	k	K	k	K		
	114	210	104	325	v_0;	S
	159	142	143	128	$1/v_0$;	$1/S$
	159	140	139	140	v_0/S	v_0

From the temperature dependence of v_0, activation parameters of the reaction cannot be calculated. Since however, the initial rate v_0 is proportional to the rate constant at a sufficiently high concentration of hydrazine, it was possible to approximate the apparent activation energy to 8 kcal/mol.

Mechanism of the Autooxidation of Hydrazine

When considering mechanism of the hydrazine autooxidation, the basic point is change in the oxidation degree of cobalt during the reaction. Formation of the yellow component characterized by an absorption maximum at 450 nm was explained[10,11] by reduction of Co(II)TSP to Co(I)TSP. It is well known that ring chelates change redox properties of the central atoms and can stabilize unusual oxidation states[3]. If reduction to Co(I)TSP took place, it would mean that hydrazine was oxidized by simple electron transfer to an intermediate, probably to a free radical N_2H_3[14,15]. This mechanism would be similar to the Haber[16] radical mechanism by which catalytic effect of cupric ions on the autooxidation of sulphite was explained. However, our experiments show that reaction of Co(II)TSP with hydrazine does not result in the formation of Co(I)TSP. The main reasons for this statement are: *a*) no relation between the redox potential of the substrates and formation of the absorption maximum at 450 nm; *b*) the continuous variation method proved formation of one, relatively strong complex of CoTSP with hydrazine. Since it has been proved that both reacting substances, oxygen as well as hydrazine, provide adducts with CoTSP reversibly, the reactive intermediate product of the autooxidation seems to be very probably the ternary complex of CoTSP with hydrazine and oxygen. The reaction mechanism is then illustrated by

$$\text{CoTSP} \underset{K_2}{\overset{K_1}{\rightleftarrows}} \begin{matrix} \text{CoTSP.O}_2 \\ \\ \text{CoTSP.N}_2\text{H}_4 \end{matrix} \underset{K_3}{\overset{K_4}{\rightleftarrows}} \text{N}_2\text{H}_4.\text{CoTSP.O}_2 \overset{k_1}{\rightarrow} \text{CoTSP + products}$$

$$(A)$$

where $K_1 - K_4$ are the equilibrium constants and k_1 the rate constant of the rate determining step. The reaction rate is proportional to the concentration of the active complex

$$-d[N_2H_4]/dt = v = k_1[N_2H_4.CoTSP.O_2] . \tag{4}$$

The total concentration of CoTSP is equal to

$$[CoTSP]_0 = [CoTSP] + [N_2H_4.CoTSP] + [CoTSP.O_2] + [N_2H_4.CoTSP.O_2] \tag{5}$$

and concentration of individual components expressed by means of equilibrium constants,

$$[CoTSP] = K_1[CoTSP][O_2] ,$$

$$[N_2H_4.CoTSP] = K_2[CoTSP][N_2H_4] ,$$

$$[N_2H_4.CoTSP.O_2] = K_2K_3[CoTSP][N_2H_4][O_2] . \tag{6}$$

After substitution into equation (4) and rearrangement we obtain

$$v = k \frac{K_2K_3[CoTSP]_0[N_2H_4][O_2]}{1 + K_1[O_2] + K_2[N_2H_4] + K_2K_3[N_2H_4][O_2]} . \tag{7}$$

Because the concentration of oxygen is constant during the experiments, equation (7) may be simplified to a form identical with equation (1) which was found to fit the experimental results. The kinetic consequences of the mechanism presumed correspond then to the kinetic course of the reaction, found experimentally. Actual meaning of the experimentally established constants results from comparison of equations (1) and (7)

$$k = k_1K_3[O_2]/(1 + K_3[O_2]) , \tag{8}$$

$$K = K_2(1 + K_3[O_2])/(1 + K_1[O_2]) . \tag{9}$$

II
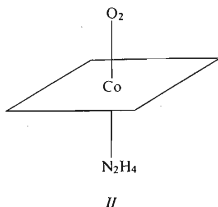
Determination of the real rate constant would be possible, provided that both equilibrium constants K_1 and K_2, or the dependence of experimentally found constant k upon $[O_2]$ are known. By using the continuous variation method, only constant $K_2 = 7 \cdot 8 \cdot 10^5$ was determined.

The kinetics of the catalyzed autooxidation of hydrazine was explained by the concept of ternary complex *II*

It is evident from the structure of the complex that electron transfer between hydrazine and oxygen is mediated by the central atom, the π-electron system of phthalocyanine ring being involved.

Oxidation of hydrazine to nitrogen as well as reduction of oxygen to water is a four-electron procedure which can occur in one or more steps. The four-electron transfer in one step is generally considered improbable, except for some enzymatically catalyzed reactions[17,18]. The assumption that reaction of hydrazine with oxygen occurs as a series of subsequent one- or two-electron processes seems therefore to be more probable. In both cases, the electron transfer is combined with proton transfers which considerably complicate concepts of the detailed reaction schema. The slowest process, determining the reaction rate, can be either splitting of the bond O—O or release of molecular nitrogen.

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