KINETICS OF THE REACTION OF COBALT(II)
TETRASULPHOPHTHALOCYANINE WITH MOLECULAR OXYGEN

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Cobalt(II) tetrasulphophthalocyanine forms in aqueous solutions an adduct with molecular oxygen, of stoichiometry $Co : O_2 = 2 : 1$. The existence of the stable adduct has been proved by measuring absorption spectra under aerobic as well as anaerobic conditions and by manometric measurements of oxygen absorption. The reaction leading to the formation of an adduct is of the 1st order with respect to CoTSP, the formation of the intermediate product $CoTSP.O_2$ being the rate determining step.

On the basis of the absorption spectra measurements it has been shown in the preliminary communication[1] that cobalt(II) tetrasulphophthalocyanine (CoTSP) forms a stable adduct with molecular oxygen. The latter may be released again from the adduct by bubbling inert gas through the solution, and the oxygenation-desoxygenation cycle can be repeated many times. The interest in the oxygen adducts of metal chelates was evocated by the effort to find suitable model substances to study oxygen transfer in biologic systems. Although Fe(II) and Cu(I) are the most common central metallic ions of natural respiratory pigments, the oxygen adducts prepared synthetically are for the most part formed by cobalt(II) complexes[2].

Similarly as with the natural oxygen carriers, two types of oxygen adducts of stoichiometry $Co : O_2 = 1 : 1$ or $2 : 1$ are known for cobaltous complexes. Mononuclear adducts are stable in a nonaqueous medium only, usually at low temperatures, while the adducts being produced in an aqueous medium are always binuclear with the oxygen bridge bond between central atoms. Recently, a series of cobaltous chelates with ligands of the polyamine[3-5] and aminoacid types[6], which produce binuclear adducts with oxygen, have been described. According to present data on the kinetics and mechanism[2] they originate following a general reaction scheme

$$CoL_n + O_2 \rightleftharpoons O_2.CoL_n , \tag{A}$$

$$O_2.CoL_n + CoL_n \rightleftharpoons L_nCo.O_2.CoL_n . \tag{B}$$
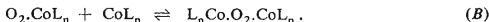
The primary reaction with oxygen, leading to the formation of an unstable intermediate, is very rapid, followed by a slow reorganization of structure to a more stable form. The reversible stabilization of the oxygen adduct is followed by a slow irreversible oxidation of the central atom, which sometimes leads even to a decomposition of the complex. Stability of the oxygen adduct towards irreversible oxidation is dependent mainly upon the nature of the ligand.

The present paper aims at finding composition of the adduct, and studying kinetics as well as mechanism of its formation.

EXPERIMENTAL

Reagents

Cobalt(II) tetrasulphophthalocyanine was prepared according to[7]. Sodium hydroxide (Merck) as well as the other reagents employed were of the A.R. grade.

Apparatus and Procedure

The absorption spectra were measured by spectrophotometer Unicam SP 800 B, in 1 cm cells, closed by a silicon rubber cap. A hypodermic syringe punctured in the rubber cover was used to introduce gas (nitrogen or oxygen) or another reagent into the cell. Nitrogen was freed of oxygen traces by passing through chromium dichloride solution and alkaline solution of hydrazine and CoTSP.

The kinetics of the formation of an adduct at CoTSP concentrations of the order of 10^{-5}M was followed at the wave-length of 670 nm using the Unicam expansion accesory. The reaction took place in the cell under air, *i.e.* at a constant oxygen concentration of $2 \cdot 5 \cdot 10^{-4}$M. The kinetic experiments at a higher CoTSP concentration of the order of 10^{-3}M were carried out in a reaction vessel equipped with a screw pump and connected to a cell 0·1 mm thick. Oxygen was admitted into the reaction vessel during the measurement so that its concentration in the solution, given by the partial pressure $p_{O_2} = 760$ Torr, amounted to $1 \cdot 23 \cdot 10^{-3}$M.

The absorption of oxygen by CoTSP solutions was measured by means of the Warburg apparatus at the temperature of $24 \cdot 95 \pm 0 \cdot 05°C$. The reaction was started by mixing the CoTSP and sodium hydroxide solutions. When studying kinetics of the absorption, the concentration of CoTSP was $2 \cdot 85 \cdot 10^{-3}$M; in the experiments involving determination of stoichiometry of the adduct, the concentration of CoTSP was altered within $1 \cdot 67 \cdot 10^{-4} - 3 \cdot 33 \cdot 10^{-3}$M. The concentration of hydroxide was always 0·5M. Prior to the mixing of the components the whole apparatus was flushed with oxygen so that the oxygen concentration in the solution was again $1 \cdot 23 \cdot 10^{-3}$M.

RESULTS AND DISCUSSION

Stoichiometry and Reversibility of the Reaction with Oxygen

Absorption spectrum of the CoTSP solutions has two typical maxima in the visible region (626 and 670 nm). (Fig. 1). In a freshly prepared alkaline solution of CoTSP, changes due to the effect of oxygen occur, which manifest themselves by an increase of the absorption maximum at 670 nm and a simultaneous decrease of the maximum at 626 nm. The limiting height of the maximum is attained according to the alkalinity of the solution within several hours or days. The spectrum of the solutions having pH < 11·6 does not change with time.

The solutions of CoTSP in dimethyl formamide $(20-60\%)$ or in ethanol $(20-90\%)$ exhibit an absorption spectrum of equal shape, as is that of aqueous alkaline solutions after attaining an equilibrium, *i.e.* with the main absorption maximum at 670 nm.

The existence of the two absorption maxima in CoTSP and some other metallic tetrasulphophthalocyanines is assigned to the presence of a monomeric as well as di-

meric form in the solution[8-10]. Since absorption is during dimerization as a rule shifted towards shorter wave-lengths[9], the maximum at 670 nm should belong to mono- meric CoTSP. This assumption is in accordance with the fact that in a nonaqueous medium, in which a shift of equilibrium towards monomer can be expected, also the maximum at the longer wave-lengths is considerably higher. According to these assumptions, however, the increase of the maximum at 670 nm, observed in alkaline solution of CoTSP, would have to belong to monomerization, which was quite unprobable. In addition, dependence of absorbance upon the CoTSP concentration obeys within $1 . 10^{-6} - 5 . 10^{-5}$M the Lambert–Beer law both in water and in 0·1M- -NaOH (Fig. 2). The shift of equilibrium between monomer and dimer would become evident by a deviation from this law and by existence of an isosbestic point.*

Since all the effects observed cannot be explained on the basis of dimerization of CoTSP, the effect of oxygen and nitrogen on the shift of the absorption maxima was further examined. Bubbling oxygen through alkaline CoTSP solution has the same effect as ageing in the air, *i.e.* increase of the maximum at 670 nm and decrease
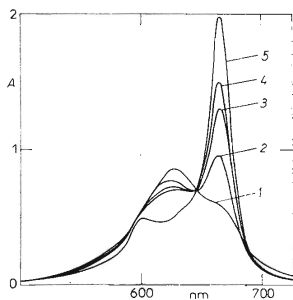

FIG. 1

Time Dependence of the Change of Ab- sorption Spectrum of CoTSP under Oxy- gen

Borate buffer pH 12·3; $1·1 . 10^{-5}$M-CoTSP; *d* 1·0 cm; *1* 0 min; *2* 60 min; *3* 190 min; *4* 310 min; *5* 4 days.
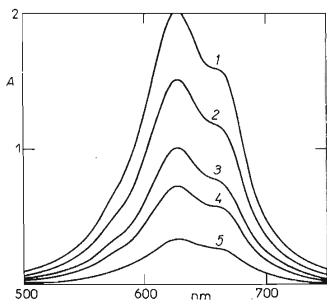
FIG. 2

Dependence of the Change of Absorption Spectrum on the CoTSP Concentration

0·1M-NaOH; *d* 1·0 cm; the curves were re- corded immediately after alkalization; con- centration of CoTSP *1* $4·0 . 10^{-5}$M; *2* 3·0 . $. 10^{-5}$M; *3* $2·0 . 10^{-5}$M; *4* $1·5 . 10^{-5}$M; *5* $7·0 . . 10^{-6}$M.

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*   As it was shown recently (Gruen L. J., Blagrove R. J.: Austr. J. Chem. *26*, 319 (1974)), absorption bands of the CoTSP-oxygen adduct and monomer occur at similar wave-lengths 670 and 663 nm respectively. It is suggested, that solutions in 0·1M-NaOH contain only oxygen adduct, dimer (626 nm) and higher aggregates.

at 626 nm, the change, however, is more rapid (Fig. 1). If nitrogen free of oxygen traces is bubbled through the solution at a temperature of 70°C, a back reaction takes place accompanied by a new rise of the maximum at 626 nm and a decrease of the maximum at 670 nm. Oxygenation as well as desoxygenation of the solution can be repeated several times without any observable irreversible change. The isosbestic point at 645 nm points to the presence of merely two absorbing components in the solution, whose mutual ratio is dependent on the oxygen concentration. From the facts presented it follows that the absorption maximum at 670 nm belongs to the oxygenated form, *i.e.*, to a CoTSP adduct with molecular oxygen, and the maximum at 626 nm to nonoxygenated CoTSP.

Formation of the CoTSP adduct with oxygen was confirmed by a manometric measurement of the amount of oxygen absorbed at different concentrations of CoTSP. The results correspond to absorption of 0.495 ± 0.012 mol of O_2 per 1 mol of CoTSP, *i.e.* to the formation of the adduct of composition $CoTSP.O_2.CoTSP$. The oxygen absorption is unusually slow and is finished only after 10 hours. For more concentrated solutions, a slight additional increase of the amount of oxygen absorbed may be observed after about 15 hours.

One of the criteria for the reversibility of the formation of the adduct is its behaviour, if pH has been changed. By acidifying the oxygenated solution, the maximum of the adduct immediately disappears in the absorption spectrum and original maximum of CoTSP reappears. After a repeated alkalization, the CoTSP adduct with oxygen is formed again. This cycle of acidification and alkalization can be repeated several times without the ability of CoTSP to bind and realese oxygen being appreciably changed. A polarographic prove of hydrogen peroxide, whose presence in an acidified solution would give evidence of a peroxidic character of the adduct, was negative.

After a longer standing of the alkaline oxygenated solution, a decrease of ab-

FIG. 3

Change of the Absorption Spectrum during Degradation of CoTSP 0·5M-NaOH; 1·0 . . 10^{-5}M-CoTSP; d 1·0 cm

1 0 min, *2* 3 h, *3* 46 h, *4* 71 h, *5* 101 h.
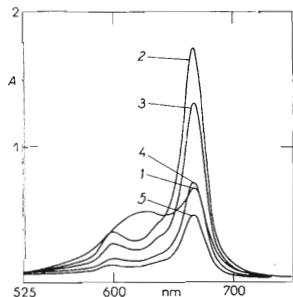
sorption begins to become evident within the whole region (580−690 nm) of the CoTSP absorption bands. The decrease of the absorption becomes evident the sooner, the higher is alkalinity of the solution. At pH = 12·8 the decrease begins to appear after a 14 days standing, in 0·1M-NaOH after 8 days, and in 0·5M-NaOH after 3 hours (Fig. 3), respectively. A complete disappearance of the absorption in the given region takes place in 0·5M-NaOH after 6 days, at lower hydroxide concentrations after several weeks. The decrease of absorption is obviously due to an irreversible oxidation of the central atom and subsequent oxidative degradation of the phthalocyanine ring; this may be assumed from the fact that not only the absorption spectrum of the adduct, but also any absorption typical for tetrasulphophthalocyanine complexes, disappears. The additional rise of the oxygen uptake after 15 hours (Fig. 4) is likely due to the oxidation of the phthalocyanine degradation products.

Kinetics and Mechanism of the Formation of CoTSP.O$_2$.CoTSP

The kinetics of the formation of CoTSP.O$_2$.CoTSP was followed spectrophotometrically in NaOH or in borate buffer, the initial concentration of CoTSP being $5 . 10^{-6}$ to $2 . 10^{-5}$M. The oxygen concentration of $2·5 . 10^{-4}$M was constant within the course of the reaction.

Since the rate of formation of the adduct is under these conditions independent of bubbling oxygen through the solution at a flow rate of 100−700 ml/min, it is apparent that the reaction is not diffusion controlled. The same conclusion has been drawn when examining the dependence upon the rate of mixing. The kinetics was examined graphically by plotting dependence of instantaneous reaction rate (v) upon
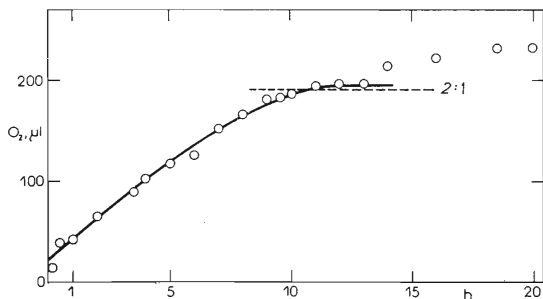

Fig. 4

Time Dependence of Oxygen Uptake
0·5M-NaOH; $2·85 . 10^{-3}$M-CoTSP.

absorbance A_t at 670 nm. The reaction rate was determined as tangent of the time dependence of A_t. The dependence of the instantaneous reaction rate upon A_t is linear up to a 60—90% conversion. An equal result is achieved by plotting log . . $(A_\infty - A_t)$ against time, where A_∞ is the absorbance after the reaction had been finished. Hence it follows that the reaction is 1st order with respect to CoTSP. The rate constants determined on the basis of these dependences are given in Table I.

It likewise follows from the Table that dependence of the rate constant on pH is very steep. At pH < 12 the reaction is virtually stopped.

The kinetics of the oxygen uptake was examined by means of a Warburg apparatus at an initial CoTSP concentration of $2·85 . 10^{-3}$M. A typical course of the reaction is illustrated in Fig. 4. The dependence of the instantaneous reaction rate (v) on concentration of oxygen absorbed by the solution corresponds up to a 60% conversion to the 1st order reaction with the rate constant $k = 2·58 . 10^{-5} \text{ s}^{-1}$.

It follows from Fig. 4 as well as from value of the rate constant that the reaction examined manometrically by measuring the oxygen uptake proceeds at considerably lower rate than in the experiments accomplished spectrophotometrically, in which, however, the initial concentration of $[\text{CoTSP}]_0$ was by two orders of magnitude lower. For this reason, the reaction kinetics was followed spectrophotometrically, at a concentration of the reaction components being the same $([\text{CoTSP}]_0 = 2·85 .$. 10^{-3}M) as in the experiments employing the Warburg apparatus. The rate constant determined in this experimental arrangement by measuring absorbance of the oxygenated form at 670 nm is $k = 7·14 . 10^{-5} \text{ s}^{-1}$. From the accordance of both values of the rate constants follows that the same reaction is investigated both spectrophotometrically and manometrically. The difference from the values obtained at the CoTSP concentrations of $5 . 10^{-6} - 2 . 10^{-5}$M is therefore not due to the measurement of different quantities, but it is caused by a higher concentration of CoTSP. As follows from the kinetic measurement presented, the absorption of oxygen, when

TABLE I

Rate Constants of the Rate Determining Step

Medium	$[\text{CoTSP}]_0$ M	k s^{-1}	$k/[\text{O}_2]$ $\text{s}^{-1} \text{ M}^{-1}$
pH 12·6	$1·00 . 10^{-5}$	$2·4 . 10^{-5}$	0·94
pH 12·8	$1·00 . 10^{-5}$	$5·98 . 10^{-5}$	2·33
pH 13·0	$1·00 . 10^{-5}$	$8·3 . 10^{-5}$	3·24
0·1M-NaOH	$1 . 10^{-6} - 4 . 10^{-5}$	$7·75 . 10^{-5}$	3·03
0·2M-NaOH	$1 . 10^{-6} - 4 . 10^{-5}$	$9·60 . 10^{-4}$	3·75
0·5M-NaOH	$1·00 . 10^{-5}$	$3·10 . 10^{-3}$	12·1

the $CoTSP.O_2.CoTSP$ adduct is being produced is relatively slow. The reaction of cobalt chelates with oxygen is usually finished within seconds or minutes; the rate determining step is, as a rule, reorganization of the intermediate $L_nCo.O_2$ to a binuclear adduct[2,4,5] so that the reaction must be of the 2nd order with respect to L_nCo. Since the reaction in the present paper is of the 1st order, the rate determining step must be the primary reaction with oxygen
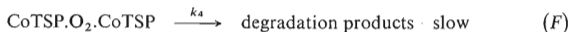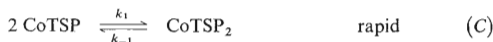
$$CoTSP + O_2 \rightarrow CoTSP.O_2$$

and not the formation of a binuclear adduct

$$CoTSP.O_2 + CoTSP \rightarrow CoTSP.O_2.CoTSP .$$

The rate determining step can also be a slow monomerization of dimer $(CoTSP)_2$. In this case, however, the rate of reaction would be independent of the oxygen concentration and the reaction would not proceed in the oxygen atmosphere more rapidly than in the air as it was observed. Consequently, relation

$$v = k[CoTSP][O_2] \tag{1}$$

holds for the rate determining step. Although absorption spectrum does not point to dimerization of CoTSP, this possibility cannot be excluded for suggesting the reaction mechanism. When studying absorption spectra in aqueous as well as nonaqueous media Fallab[8] found that ZnTSP, CuTSP, H_2TSP, and CoTSP form dimers. For CuTSP (ref.[9]) and (VO)TSP (ref.[10]), the dimerization was proved on the basis of deviations from the Lambert-Beer law. When considering all the possibilities, the following mechanism seems to be the most plausible:

$$2\ CoTSP \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CoTSP_2 \qquad \text{rapid} \tag{C}$$

$$CoTSP + O_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CoTSP.O_2 \qquad \text{slow} \tag{D}$$

$$CoTSP.O_2 + CoTSP \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} CoTSP.O_2.CoTSP \qquad \text{rapid} \tag{E}$$

$$CoTSP.O_2.CoTSP \overset{k_4}{\longrightarrow} \text{degradation products} \qquad \text{slow} \tag{F}$$

The intermediate $CoTSP.O_2$ likewise the well-known adducts with oxygen, of stochiometry 1 : 1 (ref.[2]), can be expected to be unstable in aqueous media. In addition, increase of the absorption maximum of a stable adduct (670 nm) is of equal rate as decrease of the maximum of CoTSP (626 nm); hence it follows that no accumulation of the intermediate can take place. Since, as has been shown, reaction (D) is the rate determining step it holds, after introducing the stationary state condition, that

$$d[CoTSP.O_2.CoTSP]/dt = v = k_2[CoTSP][O_2] - k_{-2}[CoTSP.O_2] - \\ - k_4[CoTSP.O_2.CoTSP] . \tag{2}$$

The third term denoting irreversible decomposition of the adduct is to be considered only at later stages of the reaction and at higher concentrations of hydroxyl ions. The second term may be neglected with respect to the first one owing to a low stationary concentration of $CoTSP.O_2$, so that the reaction can be 1st order. The lower reaction rate, observed at the CoTSP concentration of the order of $10^{-3}M$, may be accounted for the inhibiting effect of the degradation products or even of the CoTSP itself.

The $CoTSP.O_2.CoTSP$ adduct is produced, as has been said, at pH > 12 and the increase of the rate of reaction with $[OH^-]$ is very steep. Of equal character is dependence of the reaction rate in the autooxidation reactions catalyzed by CoTSP[11,12]. The expected active intermediate of these reactions is a ternary complex of a catalyst with substrate (S) and oxygen $[S.CoTSP.O_2]$, where the substrate and oxygen occupy axial coordination places. Occupation of these places seems to be possible only after dissociation of a proton whose pH must be $12-13$. Only very weakly acidic hydrogen atoms bound to the pyrolle nitrogen of the phthalocyanine skeleton could correspond to the latter value. For free phthalocyanine tetrasulphonic acid, Fallab[13] gives $pK_1 = 9.6$ and $pK_2 > pK_1$. Thus it could be possible that one of the two hydrogens bound to the pyrolle groups of tetrasulphophthalocyanine remains even in a complex with the central atom and dissociates only at a high pH. (Scheme 1).
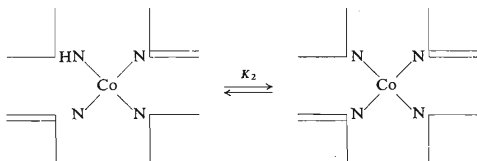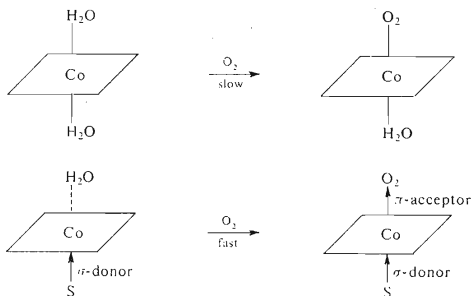

SCHEME 1

Only then, oxygen may be bound and catalytic effect of CoTSP becomes possible.

The rate constants (Table I) are lower than those of the autooxidation reactions catalyzed by CoTSP[11,12], in which the rate determining step is likely decomposition of the ternary complex $[S.CoTSP.O_2]$. Since formation of the intermediate $CoTSP.O_2$ is slower than decomposition of the ternary complex, it means that reaction (D) cannot be a step in its formation. Rapid formation of the ternary complex is a condition of the catalytic efficiency of CoTSP and may be accounted for the coordination of a nucleophylic substrate, whose presence in the *trans*-position appreciably accelerates fixation of oxygen (Scheme 2). An effect of the ligand bound to the 5th coordination place has been studied on heme in connection with the function of proximal histidine and its properties have been found to have a decisive effect on the fact, whether the oxygen is altogether bound and whether its bonding is reversible[14]. According to the Wang theory[15] verified on system $[Co.Heme.Pyridine]$ the

bonding of a strong σ-donor is responsible for the nonsymmetric splitting of the t_{2g} orbitals of a central atom, which is favourable for the formation of a bond with a π-acceptor, in the *trans*-position consequently with an oxygen molecule. The bonding

Scheme 2

of oxygen to CoTSP seems to be influenced in the same way and the ligand in the *trans*-position seems to affect not only strength of the bond, but also rate of its formation.

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