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**CATALYTIC ACTIVITY OF COBALT(II)  
TETRASULPHOPHTHALOCYANINE FOR THE OXIDATION  
OF SULPHITE IONS AND OTHER SUBSTRATES BY DIOXYGEN**

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The oxidation of sulphite ions by dioxygen in the presence of cobalt(II) tetrasulphophthalocyanine (CoTSP) is catalyzed by traces of metal ions in the system and not by the complex itself. The addition of EDTA completely suppresses the oxidation of sulphite ions even in the presence of CoTSP. When the oxidation of a substrate is actually catalyzed by CoTSP, EDTA has no effect on the reaction rate. The catalytic effect of CoTSP is observed if the substrate and the catalyst form a reactive binary adduct, CoTSP.substrate, responsible for an absorption band near 450 nm.

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Cobalt(II) tetrasulphophthalocyanine (CoTSP), and to a somewhat lesser extent Fe(III),  $\text{VO}^{2+}$ , and Mn(II) tetrasulphophthalocyanines, catalyze the oxidation of some substrates by dioxygen. The mechanism of the catalysis has been elucidated, and binary complexes of the catalyst with dioxygen and the substrate and the ternary complex  $\text{O}_2\text{.CoTSP.substrate}$  have been identified as reaction intermediates<sup>1-5</sup>. The coordination sphere of the ternary complex involves electron transfer from the substrate to dioxygen.

Because of the ecological importance of the reactions of sulphur dioxide, the oxidation of sulphite ions by dioxygen catalyzed by CoTSP was studied, and the reaction course was interpreted as catalysis by CoTSP occurring by a coordination mechanism<sup>6</sup>. Since, however, the oxidations of sulphite, ascorbic acid, and some other substrates are typical trace-catalyzed reactions<sup>7</sup>, the kinetic measurements may be affected by the presence of metal impurities in the system, for example by unremovable remainder of the free metal in the CoTSP preparation. Preliminary experiments on the autooxidation of various substrates did not reveal any catalytic effect on the oxidation of sulphite ions<sup>5</sup>.

One aim of the present work was to distinguish the catalytic effect of CoTSP from the effect of catalytically active trace metals on the oxidation of sulphite ions and other substrates. Another aim was to establish the conditions under which metal tetrasulphophthalocyanines exert their catalytic effect.

## EXPERIMENTAL

Cobalt(II) tetrasulphophthalocyanine, *i.e.* a complex of tetrasodium salt of 4,4',4'',4'''-phthalocyanine-tetrasulphonic acid with Co(II), was prepared and purified by a standard procedure<sup>8</sup>. The prescription notes that it is difficult to remove completely metal impurities from the product.

The chemicals used (Lachema) were of analytical grade, and ascorbic acid was the product of Pharmacon. Solutions of the substrates, *i.e.* of sodium sulphite, hydroxylamine hydrochloride, and ascorbic acid, were prepared fresh every other day and kept in the dark at 5°C. Disodium salt of ethylenediaminetetraacetic acid (Komplexon III, Lachema) was used to complex metal impurities.

The initial concentrations of the components in the reaction system were  $[\text{Na}_2\text{SO}_3]_0 = 3.52 \cdot 10^{-3}$  and  $1.76 \cdot 10^{-2} \text{ mol dm}^{-3}$ ;  $[\text{NH}_2\text{OH.HCl}]_0 = 3.52 \cdot 10^{-3} \text{ mol dm}^{-3}$ ; and  $[\text{ascorbic acid}]_0 = 3.52 \cdot 10^{-3} \text{ mol dm}^{-3}$ . The initial concentration of oxygen ( $\sim 2.6 \cdot 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$ ) was that corresponding to oxygen solubility in the solution under the given conditions. The concentration of EDTA was varied over the range  $8.93 \cdot 10^{-7}$  to  $4.31 \cdot 10^{-2} \text{ mol dm}^{-3}$ . The reactions were carried out in the Britton-Robinson buffer at pH = 11.5 and 20°C.

Absorption spectra of solutions in gas-tight cells 20 mm thick under a nitrogen atmosphere were measured on a Unicam 800 B instrument at pH 8.0 and 11.5.

The concentrations of oxygen and hydrogen peroxide were followed over the course of the reaction by means of a continuous amperometric analyzer of our own design<sup>9</sup>. The instrument operates on the polarographic principle using a mercury dropping electrode, and permits two components of a system to be monitored simultaneously. The instrument was calibrated with differently concentrated KCl solutions for which oxygen solubilities were known.

The reaction was run in a sealed reaction vessel with no free space over the surface of the reaction mixture, so that diffusion of oxygen from the air into the solution was excluded. The reaction was started by injecting the substrate solution or, in some cases, the catalyst solution into the reaction mixture.

The initial reaction rate,  $v_0$ , was determined by a non-linear regression of data for the oxygen concentration as a function of time to a second-degree regular polynomial in which  $v_0$  appeared as the coefficient of the linear term.

## RESULTS AND DISCUSSION

### *Effect of EDTA on the Oxidation Kinetics*

The kinetics of the oxidation of sulphite ions and reference substrates were studied by following the variations in oxygen and hydrogen peroxide concentrations in the reaction system with time.

As a result of trace-metal catalysis, the oxidation of sulphite ions occurs at a measurable rate even if no catalyst has been added. In common with similar systems, the reaction course is irreproducible<sup>7</sup>. The addition of  $8.8 \cdot 10^{-6} \text{ mol dm}^{-3}$  CoTSP results in a distinct acceleration of the reaction. An increase in the rate is also observed on addition of  $\text{Co}^{2+}$ . The uncatalyzed oxidation of sulphite ions does not occur in the presence of EDTA, which complexes traces of metal ions, thus suppressing their catalytic activity.

Next, the kinetics of sulphite oxidation were investigated in the presence of CoTSP. The dependences of the initial reaction rate,  $v_0$ , on the EDTA concentration for two initial sulphite concentrations are represented in Fig. 1. The initial rate is seen to decrease steeply with increasing concentration of EDTA. The reaction stops completely at EDTA concentrations of the order of  $10^{-4}$  mol dm $^{-3}$ .

No hydrogen peroxide formation was observed during the sulphite oxidation. Taking into account the sensitivity of the above method of determination,  $[\text{H}_2\text{O}_2] < 5 \cdot 10^{-5}$  mol dm $^{-3}$ . Since the two-electron oxidation of sulphite ions must be assumed to involve the intermediate formation of hydrogen peroxide, it follows that the consecutive reactions of hydrogen peroxide are sufficiently rapid even without any added catalyst.

The kinetics of the oxidation of hydroxylamine and ascorbic acid were investigated under the same conditions as used in the sulphite oxidation. The oxidations of the two substrates are undoubtedly catalyzed by CoTSP<sup>1,2,4,5</sup>, and are at the same time trace catalyzed reactions. Fig. 1 includes a plot of  $v_0$  against the EDTA concentration for both the above substrates with CoTSP present. For hydroxylamine, the addition of EDTA has no effect on the rate of CoTSP-catalyzed oxidation. In the case of ascorbic acid, where the effect of trace catalysis is more pronounced, there is first a slight decrease in the initial reaction rate but further increase of EDTA concentration has no effect on the reaction rate. The decrease in the initial reaction rate produced by EDTA addition corresponds to elimination of the contribution of the trace catalyzed reaction to the overall rate of the catalyzed reaction. Once the catalytic effect of impurities is eliminated by added EDTA, the only reaction occurring is that catalyzed by CoTSP whose rate, as in the case of hydroxylamine, is independent of EDTA concentration.

In the oxidations of hydroxylamine and ascorbic acid, the formation of hydrogen peroxide was observed. Its concentration passed through a maximum and then decreased as a consequence of a slow reaction with the substrate, also catalyzed by CoTSP<sup>4</sup>.

#### *Absorption Spectra of the Reaction System*

Fig. 2 shows the absorption spectrum of CoTSP (curve 1). The absorption bands are characteristic of the monomeric ( $\lambda = 670$  nm) and dimeric ( $\lambda = 626$  nm) forms of CoTSP, which are in a mobile equilibrium<sup>10</sup>. The addition of hydrazine, hydroxylamine, cysteine, ascorbic acid or some other substrates under anaerobic conditions gives rise to a new maximum near 450 nm characteristic of the binary adduct CoTSP.substrate<sup>1,4,5</sup> and causes a reduction in the intensity of the initial absorption bands (Fig. 2, curves 2–4; Fig. 3, curve 3). The oxidation of the above substrates by dioxygen is catalyzed by CoTSP, the binary adduct CoTSP.substrate being the reaction intermediate<sup>1,4,5,11</sup>.

To eliminate the possibility that the added EDTA decreases the catalytic activity of CoTSP by occupying the axial coordination sites accessible to substitution, we have measured absorption spectra of CoTSP and the binary adduct CoTSP.substrate in the absence and with an excess of EDTA. The effect of EDTA on the spectra of CoTSP and the CoTSP.ascorbic acid adduct is shown in Fig. 3. The same pattern was observed for hydrazine, hydroxylamine, and cysteine. None of the spectra gave any indication of an interaction with EDTA. The EDTA does not affect the equilibrium between the dimeric ( $\lambda = 626 \text{ nm}$ ) and monomeric ( $\lambda = 670 \text{ nm}$ ) forms of CoTSP, which is a sensitive indicator of the interference of another ligand, nor does it compete with the intermediate formation ( $\lambda = 450 \text{ nm}$ ). EDTA bound through a single functional group to the axial coordination site of CoTSP is a weak complexing agent. Moreover, the bonding of a bulky ligand to a coordination site hindered by the tetrasulphophthalocyanine skeleton is sterically unfavourable. There is therefore no reason to believe that the presence of EDTA affects the catalytic activity of CoTSP.

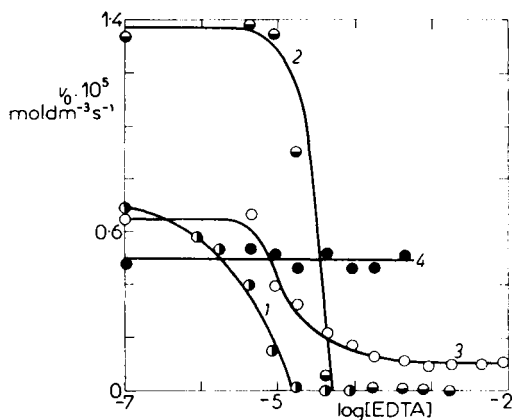


FIG. 1

Dependence of the initial reaction rate,  $v_0$ , on EDTA concentration.  $[\text{CoTSP}] = 8.8 \cdot 10^{-6} \text{ mol dm}^{-3}$ ;  $[\text{O}_2]_0 = 2.37 \cdot 10^{-4}$  to  $2.72 \cdot 10^{-4} \text{ mol dm}^{-3}$ , depending on the solution composition; Britton-Robinson buffer,  $\text{pH} = 11.5$ ; 1  $[\text{Na}_2\text{SO}_3]_0 = 3.52 \cdot 10^{-3} \text{ mol dm}^{-3}$ ; 2  $[\text{Na}_2\text{SO}_3]_0 = 1.76 \cdot 10^{-2} \text{ mol dm}^{-3}$ ; 3  $[\text{ascorbic acid}]_0 = 3.52 \cdot 10^{-3} \text{ mol dm}^{-3}$ ; 4  $[\text{hydroxylamine}]_0 = 3.52 \cdot 10^{-3} \text{ mol dm}^{-3}$

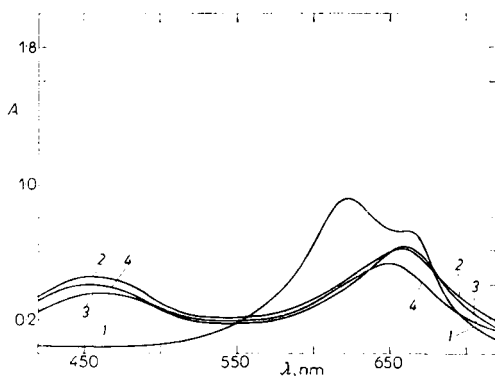
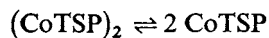


FIG. 2

Changes in the absorption spectrum of CoTSP produced by addition of catalytically oxidizable substrates.  $[\text{CoTSP}] = 9.5 \cdot 10^{-6} \text{ mol dm}^{-3}$ ;  $\text{N}_2$  atmosphere;  $0.1 \text{ mol dm}^{-3} \text{ NaOH}$ ; 1 CoTSP alone; 2  $7.62 \cdot 10^{-3} \text{ mol dm}^{-3}$  hydrazine; 3  $7.62 \cdot 10^{-3} \text{ mol dm}^{-3}$  hydroxylamine; 4  $7.62 \cdot 10^{-3} \text{ mol dm}^{-3}$  cysteine,  $\text{pH} = 9.1$

Fig. 4 shows how the absorption spectrum of CoTSP changes in the presence of sulphite ions. The interaction with sulphite ions results in growth of the band due to the CoTSP monomer ( $\lambda = 670$  nm) and a decrease in the intensity of the band of the dimer ( $\lambda = 626$  nm); no absorption band at 450 nm appears in the interaction with sulphite ions. The described change is different from spectral changes produced by substrates accessible to catalytic oxidation (Fig. 2). The sulphite ions only cause the monomer-dimer equilibrium



to shift in favour of the monomer. The spectral change due to the sulphite addition was observed in an atmosphere of nitrogen. This excluded the possibility of formation of the stable adduct with dioxygen,  $\text{CoTSP}\cdot\text{O}_2\cdot\text{CoTSP}$ , which also absorbs at 670 nm<sup>12</sup> and whose absorption band could be confused with that of the monomer<sup>13</sup>.

If oxygen is introduced into an alkaline solution of sulphite and CoTSP (pH = 11.5), the maximum at 670 nm further increases in intensity because the adduct with dioxygen is formed. At pH = 8, where no formation of the adduct occurs<sup>12,14</sup>, the maximum at 670 nm decreases in intensity as a result of sulphite oxidation and a shift of the equilibrium back in favour of the dimer.

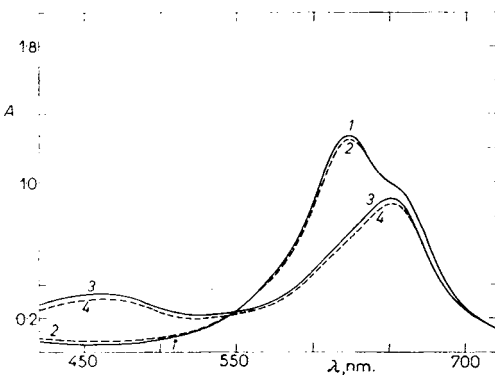


FIG. 3

Effect of EDTA on the absorption spectra of CoTSP and the intermediate CoTSP.ascorbic acid.  $[\text{CoTSP}] = 1.14 \cdot 10^{-5}$  mol  $\cdot$  dm<sup>-3</sup>, N<sub>2</sub> atmosphere; pH = 11.5; 1 no EDTA; 2  $3.04 \cdot 10^{-4}$  mol dm<sup>-3</sup> EDTA; 3  $2.99 \cdot 10^{-3}$  mol dm<sup>-3</sup> ascorbic acid, no EDTA; 4  $2.99 \cdot 10^{-3}$  mol dm<sup>-3</sup> ascorbic acid,  $3.04 \cdot 10^{-4}$  mol dm<sup>-3</sup> EDTA

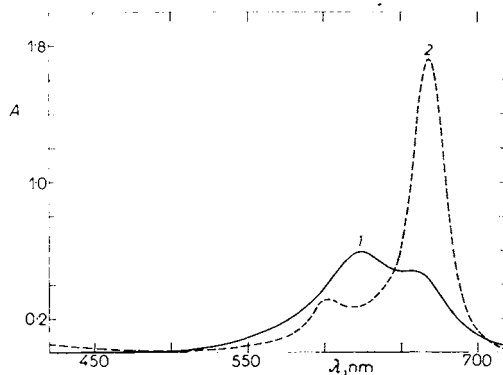


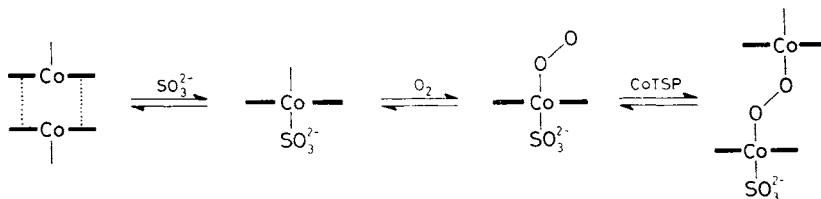
FIG. 4

Change in the absorption spectrum of CoTSP produced by addition of sulphite ions.  $[\text{CoTSP}] = 5.85 \cdot 10^{-6}$  mol dm<sup>-3</sup>; N<sub>2</sub> atmosphere; pH = 11.5; 1 no sulphite; 2  $2.975 \cdot 10^{-3}$  mol dm<sup>-3</sup> Na<sub>2</sub>SO<sub>3</sub>

### Catalytic Activity of CoTSP

The kinetic experiments as well as the absorption spectra of the system indicate that the catalytic activity of CoTSP for the oxidation by dioxygen is not affected by EDTA. It follows that the oxidation of sulphite ions which, unlike the reactions of hydroxylamine and ascorbic acid, can be completely suppressed by the addition of EDTA, is not catalyzed by CoTSP. The only catalysts are metal impurities, whose catalytic activity is suppressed by added EDTA. Metal ions may also be introduced into the system with the addition of CoTSP and the catalytic activity observed may be mistaken for that of CoTSP (ref.<sup>6</sup>).

The increase in the intensity of the absorption band of CoTSP monomer on addition of sulphite ions (Fig. 4) suggests that the sulphite occupies the free axial coordination site, thus favouring the dissociation of the dimer. It is well known that a ligand bound to the axial coordination site promotes the bonding of dioxygen at the *trans* position and the more so the stronger its donor properties<sup>15</sup>. In the presence of sulphite ions, if their oxidation is suppressed by added EDTA, the intensity of the maximum due to the stable adduct with dioxygen, CoTSP.O<sub>2</sub>.CoTSP, increases far more rapidly than it does in the absence of sulphite ions, in which case the axial coordination sites are occupied by water molecules or hydroxyl ions. The interaction of CoTSP with sulphite ions is represented in Scheme 1, where the heavy solid lines



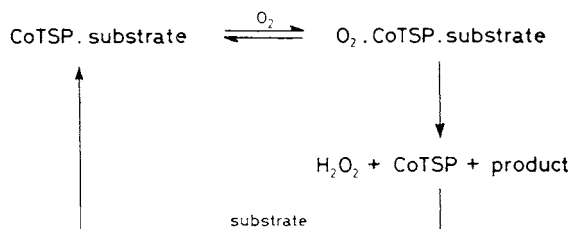
SCHEME 1

indicate the plane of the phthalocyanine ligand occupying four equatorial coordination sites. The ternary complex O<sub>2</sub>.CoTSP.SO<sub>3</sub><sup>2-</sup> is unreactive, no electron transfer or sulphite oxidation occurring within its coordination sphere. Despite making the same assumption, Boyce and coworkers<sup>6</sup> unjustifiably ascribe the sulphite oxidation to a catalytic effect of CoTSP. The lack of reactivity of the ternary complex O<sub>2</sub>.CoTSP.SO<sub>3</sub><sup>2-</sup> is the reason why CoTSP alone fails to catalyze the sulphite oxidation, although this reaction might be expected to occur considering the entry of the sulphite ion into the coordination sphere of the complex and the oxidation-reduction potential of the sulphite ion ( $E_B^0 = -0.93$  V (ref.<sup>16</sup>)). Cyanide, imidazole, and thiodiglycol show the same behaviour as sulphite<sup>17</sup>.

The catalytic activity of CoTSP is correlated with an absorption band that appears at 450 nm on addition of the substrate. This absorption band arising from a reaction

intermediate has been ascribed, on the basis of absorption<sup>4,5</sup> and ESR<sup>14</sup> spectra, to the binary adduct CoTSP.substrate. The alternative explanation that the intermediate is Co(I)TSP resulting from reduction by the substrate, contradicts the stoichiometry of the CoTSP-substrate interaction.<sup>4,5,11</sup> According to this assumption, the absorption bands in the same region observed for reactions catalyzed by Fe(III)TSP and Mn(II)TSP should correspond to Fe(I)TSP and Mn(I)TSP intermediates. Their existence is, however, highly improbable and the results suggest that Fe(II)TSP.substrate and Mn(II)TSP.substrate adducts are formed. The absorption bands of a tetrasulphophthalocyanine are "ligand" bands originating in electron transfers between the molecular orbitals of the ligand. Their positions and intensities are little affected by the nature of the central ion<sup>18</sup>.

The ternary complex produced by a rapid reaction of the reactive binary adduct CoTSP.substrate with dioxygen is also reactive and decomposes to give the oxidation product and hydrogen peroxide (Scheme 2). The reactive binary intermediate is



SCHEME 2

formed by coordination of the substrate, which causes a substantial change in the electron density distribution within the complex. This change brings about a shift of the absorption maximum by about 200 nm to shorter wavelengths. Correlation of this shift with kinetic measurements of the oxidation of sulphite ions and other substrates shows that the catalytic effect of CoTSP on the oxidation by dioxygen is present for only those substrates which coordinate to CoTSP to form a reactive binary intermediate characterized by an absorption band at 450 nm.

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