FAST REACTION STEPS AND INTERMEDIATES OF THE OXIDATION OF ASCORBIC ACID BY DIOXYGEN. CATALYSIS BY COBALT(II) TETRASULPHOPHTHALOCYANINE

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The oxidation of ascorbic acid by dioxygen catalyzed by cobalt(II) tetrasulphophthalocyanine (CoTSP) has been studied by the stopped-flow method. Two reactive intermediates, $[O_2.CoTSP.$ ascorbic acid] and $[O_2.CoTSP]$, characterized by separate absorption bands at 570 nm and 634 nm, respectively, have been proved to form in the reaction. The individual steps of the reaction have been elucidated, and their rate constants have been determined or estimated.

Kinetic data obtained in studying several reactions of dioxygen catalyzed by metal ions and complexes have suggested that these reactions proceed by the coordination mechanism involving mixed-ligand complexes of the type $[O_2.catalyst.substrate]$ as intermediates[1,2].

In a previous work[3] we proved that the oxidation of ascorbic acid by dioxygen catalyzed by vanadyl tetrasulphophthalocyanine (VOTSP) proceeds *via* the mixed-ligand complex $[O_2.V(III)TSP.ascorbic acid]$ as reactive intermediate. In this case the circumstances were favourable for obtaining the evidence, since VOTSP is not a very efficient catalyst, and, consequently, the stationary concentration of the reactive intermediate is sufficient. Moreover, like the other ring chelates, VOTSP has a high molar absorption coefficient (of the order of 10^5) allowing mixed-ligand complexes of the catalyst with the reaction components to be identified even when present in low concentrations.

In the present work, the oxidation of ascorbic acid by dioxygen was catalyzed by cobalt(II) tetrasulphophthalocanine (CoTSP), which is known to be an effective catalyst for some direct oxidations by dioxygen[1,2] and for induced oxidations (cooxidations)[4]. The aim of this work was to identify reactive intermediates, and to investigate the kinetics of the fast elementary steps of this reaction.

EXPERIMENTAL

Chemicals. The cobalt(II) tetrasulphophthalocyanine tetrasodium salt was prepared and purified as described previously[5]. The stock solutions of ascorbic acid (Farmakon, Czechoslovakia, Index Pharm 3) were prepared fresh every other day, and kept in the dark at 5°C. All the other chemicals used were of analytical grade.

Static absorption spectra were taken using a Unicam SP 800 B instrument.

Kinetic measurements were carried out on a Durrum D-100 stopped-flow spectrophotometer using a cell of 2 cm thickness. The reaction was started by a change in pH except some cases where ascorbic acid or an oxygen-saturated solution was added to an oxygen-free mixture of the other reaction components. In the latter case, the initial oxygen concentration in the reaction mixture was $1.25 \cdot 10^{-4}$ mol l^{-1}. In experiments carried out in the absence of oxygen, the whole flow system of the apparatus was first evacuated and flushed with nitrogen. The solution in the stock syringe was deoxygenated by bubbling with nitrogen. The experiments in argon atmosphere were performed on a double-beam stopped-flow spectrophotometer built in J. Heyrovský Institute of Physical Chemistry and Electrochemistry[6], using a cell of 1 cm thickness. The instrument had been designed to be capable of maintaining highly anaerobic conditions. The reaction was run in 0.25M-NaOH at 25°C. The catalyst concentration was varied in the range $2.5 \cdot 10^{-6}$ to $1 \cdot 10^{-5}$ mol l^{-1}. The ascorbic acid concentration ranged from $2 \cdot 10^{-3}$ to $2 \cdot 10^{-2}$ mol l^{-1}. The concentration of oxygen was that given by its solubility at atmospheric pressure, *i.e.* $2.5 \cdot 10^{-4}$ mol l^{-1}. In experiments with sulphuric acid additions, the acid concentration in the reaction mixture was within $1-2$ mol l^{-1}. The binary adduct of CoTSP with ascorbic acid, CoTSP.A, was prepared by mixing the two components and alkalining the solution under rigorous exclusion of oxygen. The adduct with dioxygen was prepared by allowing a solution of CoTSP in 0.5M-NaOH to stand in air for 2 h, at which time maximum concentration of the stable adduct was attained[7]. Each kinetic curve at a given wavelength and reaction conditions was recorded at $5-6$ time resolutions in the region $5 \cdot 10^{-3}-5$ s/cm.

RESULTS AND DISCUSSION

Reaction System

The static absorption spectra of the reaction system CoTSP–ascorbic acid–O$_2$ under various conditions are shown in Fig. 1. Since CoTSP reacts with both ascorbic acid and dioxygen in an alkaline medium only, the kinetic runs could conveniently be started by a change in pH, *i.e.* by an addition of NaOH. The absorption band wavelengths for the individual components (CoTSP monomer, (CoTSP)$_2$ dimer, the adduct with the substrate, CoTSP.A, and the stable adduct with dioxygen, CoTSP.O$_2$. .CoTSP), and the molar absorption coefficients are listed in Table I. The data show that the absorption bands due to the monomer and the stable adduct with dioxygen are too closely spaced to be resolved. The molar absorption coefficients were obtained from static absorption spectra recorded under conditions where the concentrations of the measured components were maximum. In the case of the adduct with dioxygen, there is practically no monomer in the solution under the given conditions[8].

The strategy of the kinetic experiments was based on the reaction Scheme 1 (A — ascorbic acid) envisaged on the basis of previous experiments[1−3].

The reaction kinetics were followed in several series of experiments using CoTSP (a mixture of monomer and dimer), the binary adduct with the substrate, CoTSP.A or the stable adduct with dioxygen, CoTSP.O$_2$.COTSP, as starting forms of catalyst.

In addition, we followed the reaction in the absence of oxygen, *i.e.* the partial system corresponding to the lower part of Scheme 1, and the reaction in the absence of as-
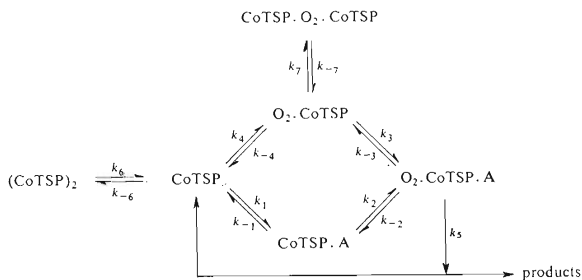
SCHEME 1

corbic acid corresponding to the upper part of Scheme 1. The absorbance–time kinetic curves were recorded at wavelengths corresponding to absorption bands of the individual components. The stopped-flow method was used to follow the kinetics of the
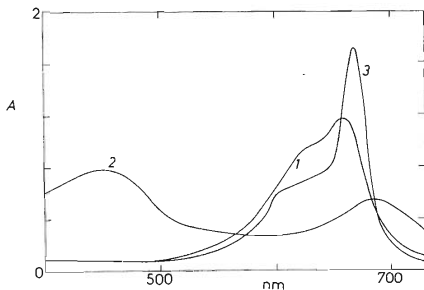

FIG. 1

Absorption spectrum of the system CoTSP–ascorbic acid–O_2. Cell of 2 cm thickness. *1* $1 . 10^{-5}$M--CoTSP, *2* $1 . 10^{-5}$M-CoTSP; 0·25M-NaOH; $1 . 10^{-2}$M-ascorbic acid; N_2 atmosphere. *3* $1 .$. 10^{-5}M-CoTSP; 0·25M-NaOH; after 10 min of bubbling with O_2

catalyst–ascorbic acid–dioxygen interaction in the initial stages of the reaction, and not the kinetics of the loss of reactants. *i.e.* of oxygen and ascorbic acid.

The system CoTSP–O_2–*Ascorbic Acid*. In the first series of experiments, the starting form of the CoTSP catalyst was an equilibrium mixture of monomer and dimer, and the reaction was started by making the solution alkaline. The kinetic curves recorded at 626 nm ($(CoTSP)_2$) and 450 nm (CoTSP.A) are the mirror images of each other, with the ascending phase of one curve corresponding to the descending phase of the other and *vice versa* (Fig. 2a,c). This behaviour corresponds to a decrease in the concentration of the dimer in favour of the adduct CoTSP.A which is an intermediate and, because of the excess of ascorbic acid, at the same time one of the products of the reaction after the consumption of oxygen. The mutual correspondence of the phases of both curves reflects the mobility of the monomer–dimer equilibrium.

The search for the absorption band due to the assumed reaction intermediate was carried out by recording the kinetic curves in dependence on wavelength which was varied in steps of $5-10$ nm in the region $450-690$ nm. The curves exhibiting maxima characteristic of the intermediate were found in the wavelength region $565-575$ nm. The highest maximum in the curve was observed at 570 nm so that the absorption band of the intermediate is apparently centered at this wavelength (Fig. 2b). The position of the maximum and the principal (descending and ascending) phases of this curve correspond to the phases of absorbance of the starting compound and of the adduct CoTSP.A. With increasing concentration of ascorbic acid, the inflexion points of the curves at 626 and 450 nm, and the maximum at 570 nm shift to longer times; the mutual correspondence of the curves is retained.

The runs with the adduct CoTSP.A as starting form of catalyst were started by adding an oxygen-saturated solution. The kinetic curves were recorded at 450 nm (CoTSP.A), 570 nm (intermediate), 626 nm ($(CoTSP)_2$), and 670 nm (CoTSP +

TABLE I

Absorption bands and molar absorption coefficients of the reaction components

Component	λ nm	ε $l\ mol^{-1}\ cm^{-1}$
$(CoTSP)_2$	626	$1 \cdot 9 \cdot 10^5$
CoTSP	663 (ref.[8])	$(1 \cdot 03 \pm 0 \cdot 01) \cdot 10^5$ (ref.[9])
CoTSP.A	450	$2 \cdot 4 \cdot 10^4$
$CoTSP.O_2.CoTSP$	670	$3 \cdot 3 \cdot 10^5$

+ CoTSP.O_2.CoTSP). The curves had practically the same shapes as found in the case of CoTSP as the starting form (Fig. 2); the only difference was that the inflexion points on the curves at 450 and 626 nm, and the position of the maximum due to the intermediate (570 nm) were shifted to shorter times, and that the short initial segments did not appear. Since practically all of the catalyst was present as the adduct CoTSP.A at the onset of the experiment, it would have been expected that the initial part of the curve at 450 nm would be descending (decrease in CoTSP.A) while that of the curve at 626 nm would be ascending (increase in (CoTSP)$_2$). That this reaction phase is unobservable by the stopped-flow method is indicative of the high rate at which the starting form of the catalyst is regenerated by the reaction of CoTSP.A with oxygen which is present in excess at the beginning of the reaction. This means, with regard to the dead time of the instrument, that the half life of the reaction $t_{1/2} < 2 \cdot 10^{-3}$ s.

In a further series of experiments, the initial form of catalyst was the stable adduct with dioxygen, CoTSP.O_2.CoTSP, and the reaction was started by adding ascorbic acid. The curves registered at the individual wavelengths have again essentially the same shapes as those shown in Fig. 2, with the inflexion points shifted to longer times. When the reaction was started by an addition of sulphuric acid, the only result of the pH change was decomposition of the adduct with dioxygen. Since practically no CoTSP monomer, which also absorbs at 670 nm, was present at the
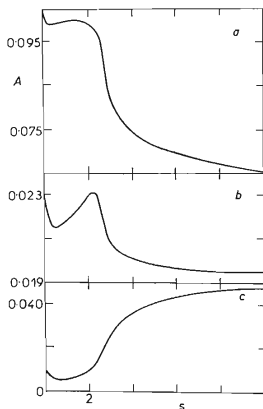

Fig. 2

Variation in absorbance with time in the system CoTSP–ascorbic acid–O_2. $2 \cdot 5 \cdot 10^{-6}$M--CoTSP; $1 \cdot 10^{-2}$M-ascorbic acid; $0 \cdot 25$M--NaOH; $2 \cdot 5 \cdot 10^{-4}$M-O_2. Time resolution 1 s/cm. a $\lambda = 626$ nm (CoTSP)$_2$, b $\lambda = 570$ nm (O_2.CoTSP.A), c $\lambda = 450$ nm (CoTSP.A)

beginning of the reaction, the initial phase of decreasing absorbance at 670 nm corresponds to the decomposition of the stable adduct with dioxygen.

The partial system CoTSP–O_2. The reaction between CoTSP and dioxygen in the absence of ascorbic acid was started by a change in pH. The kinetic curves recorded at 670 nm (CoTSP + CoTSP.O_2.CoTSP) and 626 nm ((CoTSP)$_2$) are shown in Figs 3a,b and 4a,b respectively. Unlike the curves obtained in the presence of ascorbic acid, the curve at 670 nm exhibits a decrease while the curve at 626 nm an increase in the initial part. The subsequent very slow phases of the curves in Figs 3a and 4a correspond to slow formation of the stable adduct with dioxygen, CoTSP.O_2.CoTSP (ref.[7]). The curve registered at 570 nm in the absence of ascorbic acid showed no variation in absorbance with time, thus giving no evidence for the existence of an intermediate. The formation of the stable binuclear adduct with an oxygen bridge requires that an unstable adduct with a metal : O_2 molar ratio of 1 : 1 be first formed as intermediate[10]. The unstable adduct was detected by recording kinetic curves in dependence on wavelength varied in steps of 2–5 nm. The kinetic curve with a maximum characteristic of the intermediate was found at 634 nm (Fig. 4c).
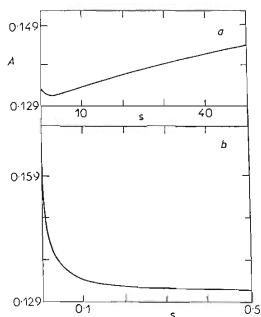

FIG. 3

Variation in absorbance with time in the system CoTSP–O_2. $2.5 . 10^{-6}$M-CoTSP; 0·25M-NaOH; $2.5 . 10^{-4}$M-O_2. $\lambda = 670$ nm (CoTSP monomer + CoTSP.O_2.CoTSP). *a* time resolution 5 s/cm *b* time resolution 0·05 s/cm
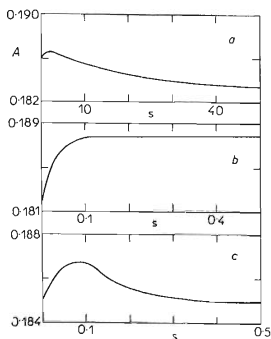
FIG. 4

Variation in absorbance with time in the system CoTSP–O_2. $2.5 . 10^{-6}$M-CoTSP; 0·25M-NaOH; $2.5 . 10^{-4}$M-O_2. *a* $\lambda = 626$ nm (CoTSP)$_2$; time resolution 5 s/cm; *b* $\lambda = 626$ nm (CoTSP)$_2$; time resolution 0·05 s/cm; *c* $\lambda = 634$ nm (O_2.CoTSP) time resolution 0·05 s/cm

A change in pH together with a change in the ionic strength of the solution may produce a shift in the equilibrium between the monomer and the dimer, which would be reflected in the kinetic curve. Therefore, we followed the reaction of CoTSP with NaOH under an atmosphere of nitrogen by recording the curves at 626 nm and 670 nm (CoTSP monomer). At 634 nm, no variation in the absorbance with time was observed in the absence of oxygen. It was only on admission of air into the apparatus that a poorly developed maximum appeared at 0·09 s (Fig. 4c). Kinetic curves at 626 nm and 670 nm exhibit the same initial rapid phase as observed in Figs 3 and 4, which, therefore, may be assigned to a shift in the equilibrium in favour of the dimer. With increasing concentration of CoTSP, the reaction is accelerated in accordance with the above interpretation. Kinetic curves of the same character were also observed in following the reaction between CoTSP and sulphuric acid, which implies that an increase in the ionic strength on changing pH in the opposite direction likewise produces a shift in the equilibrium in favour of the dimer. This is consistent with the concept of the character of intermolecular forces responsible for the dimerization of phthalocyanine complexes[11].

The partial system CoTSP–*Ascorbic Acid.* The reaction of CoTSP with ascorbic acid in the absence of oxygen was run under an atmosphere of argon, and started by a change in pH (alkalinization). A special apparatus[6] had to be employed because the system is sensitive to even traces of oxygen. Again, kinetic curves were recorded at 670 nm (CoTSP monomer), 626, 570 and 450 nm. At 570 nm, no change due to the formation of the intermediate was detected. Thus, the appearance of the maximum on the curve at 570 nm is associated with the presence of both oxygen and ascorbic acid. The rate of the descending phase at the beginning of the curve at 670 nm (decrease in the monomer) corresponds to the rate of the ascending phase of the curve at 450 nm (increase in CoTSP.A). The corresponding rate was observed at the beginning of the curve taken at 626 nm (decrease in the dimer). As both the monomer and the dimer are present at the beginning of the reaction, the observation points to a considerable rate of monomerization.

Curve Interpretation and Rate Constant Determination

Since oxygen is initially in an excess over catalyst, and ascorbic acid in an excess over both catalyst and oxygen throughout the reaction, most of the reaction steps are unimolecular or pseudo-unimolecular. Some of the rate constants may therefore be estimated from reaction half lives measured within the parts of kinetic curve corresponding to a single reaction predominating. Other rate constants have been calculated from the instantaneous reaction rates; the underlying assumptions regarding the concentrations of the individual components are specified below.

Considering the corresponding phases of the curves at 626 and 450 nm, the curve at 570 nm (Fig. 2), and the variation in the character of the curves with the wave-

length, we may conclude that the curve recorded at 570 nm is characteristic of an inter-mediate with an absorption band at 570 nm. Since this absorption band only appears when all the components, *i.e.* the catalyst, oxygen and ascorbic acid, are present, it seems justified to conclude that the intermediate is a reactive mixed-ligand complex $[O_2.CoTSP.A]$. The position of the absorption band between the bands due to the catalyst and the adduct of the catalyst with the substrate is analogous to that observed in the case of the reaction system catalyzed by vanadyl tetrasulphophthalo-cyanine[3].

The shape of the kinetic curves remains unchanged whether CoTSP.A or CoTSP was the initial form of catalyst, indicating a considerable reaction rate at which CoTSP must be regenerated on adding oxygen to CoTSP.A. The regeneration may occur by three pathways, namely by the decomposition of the mixed-ligand com-plex to reaction products and the catalyst, by the reverse reaction marked k_{-1}, and by following the path involving the mixed-ligand complex and the unstable adduct with dioxygen. The last pathway is undoubtedly the fastest since the decom-position of the mixed-ligand complex to products is mostly the rate-determining step in the system, and the reverse reaction k_{-1} does not occur in the presence of excess ascorbic acid. The rate constant k_2 for the reaction CoTSP.A + $O_2 \rightarrow O_2$. .CoTSP.A was determined from the initial part of the curve recorded at 470 nm to be $k_2 = 1·1 . 10^6 \, l \, mol^{-1} \, s^{-1}$.

The rate constant k_5 of the rate-controlling reaction was determined from the last sections of the curves recorded at 626, 570, and 450 nm. The values obtained agree, within experimental error, with one another, and are independent of the ascorbic acid concentration, which is consistent with the above mechanism. The average value $k_5 = 1·23 \, s^{-1}$.

As indicated by the reaction of CoTSP with NaOH under nitrogen, the initial phases of the curves at 670 and 626 nm in the absence of ascorbic acid (Figs 3*b*, 4*b*) are due to a shift in the equilibrium between the monomer and the dimer in favour of the dimer. The shape of this part of the curve is the same both in the presence of oxygen and in an atmosphere of nitrogen. The decrease in the concentration of monomer in the initial stages of the reaction is given by

$$d[CoTSP]/dt = -2k_{-6}[CoTSP]^2 . \qquad (1)$$

The initial monomer concentration was calculated on the basis of the equilibrium constant of dimerization, $K = [(CoTSP)_2]/[CoTSP]^2 = 2 . 10^5 \, l \, mol^{-1}$ (ref.[9,12]). The rate constant of dimerization, k_{-6}, was calculated from the measured reaction half life, according to the relation $t_{1/2} = 1/k_{-6}[CoTSP]$ which holds for the above type of second-order reaction. The values of the rate constant obtained both in the presence of oxygen and under nitrogen agree, within experimental error, with each other. The average value $k_{-6} = 6·2 . 10^7 \, l \, mol^{-1} \, s^{-1}$, and hence, using the above

equilibrium constant, $k_6 = 3 . 10^2 \, \mathrm{s}^{-1}$. The rate constant determined on the basis of the experiments with equilibrium shifted by an addition of sulphuric acid is $8 \cdot 5 . 10^7 \, \mathrm{l \, mol^{-1} \, s^{-1}}$. Both the k_6 and k_{-6} values are by several orders of magnitude higher than those quoted in the literature[9] for infinite dilution and ionic strength $I \approx 0$. The difference in the values is considerable, but might be attributed to differences in the reaction conditions. If the pre-equilibrium were so immobile as indicated by the literature data, the reaction system could not behave as observed.

The rate constant k_1 for the reaction $\mathrm{CoTSP + A \rightarrow CoTSP.A}$ was determined from results of the experiments carried out under an atmosphere of argon, and started by a change in pH, *i.e.* by alkalining a mixture of CoTSP and ascorbic acid. The reaction half life was taken from the initial phases of the kinetic curves measured at 670 nm (decrease in the CoTSP monomer), and 450 nm (increase in CoTSP.A). Since the measured half life, $t_{1/2} \approx 3 \cdot 6 . 10^{-3} \, \mathrm{s}$, is comparable with the dead time of the mixing chamber, it is possible that the rate constant $k_1 = 1 \cdot 9 . 10^4 \, \mathrm{s}^{-1}$ calculated from the $t_{1/2}$ is lower than the true value. In these experiments, the curves taken at 670 nm (CoTSP monomer) and 626 nm ((CoTSP)$_2$) show an initial decrease; the shift in the equilibrium in favour of the dimer, observed on alkalining the CoTSP solution, does not occur here, which implies that the reaction rate of dimerization, v_{-6}, must be lower than v_1. No evidence for the shift in the equilibrium in favour of the dimer has been found either in the experiments carried out in the presence of both oxygen and ascorbic acid: the kinetic curve at 626 nm ((CoTSP)$_2$) starts with a decrease (Fig. 2a) while that at 670 nm (CoTSP + CoTSP.O$_2$.CoTSP) exhibits an initial increase arising apparently from a rapid increase in the stable adduct with dioxygen formed in the mobile reaction path *via* the mixed-ligand complex. Even in this case it must hold that $v_{-6} < v_1$, since the reaction of CoTSP with dioxygen is slow. The reaction rates are given as

$$v_{-6} = 2k_{-6}[\mathrm{CoTSP}]^2 \, . \tag{2}$$

$$v_1 = k_1[\mathrm{CoTSP}][\mathrm{A}] \, . \tag{3}$$

Considering the equilibrium concentration [CoTSP] at the start of the reaction, the rate constant k_1 can be estimated from experiments under both argon and oxygen as about $2 . 10^5 \, \mathrm{l \, mol^{-1} \, s^{-1}}$.

In following the reaction of CoTSP with dioxygen yielding the stable adduct CoTSP.O$_2$.CoTSP, we detected the intermediate formation of the unstable adduct with dioxygen, O$_2$.CoTSP, showing an absorption band at 634 nm. Neglecting the term $k_{-7}[\mathrm{CoTSP.O_2.CoTSP}]$, the instantaneous reaction rate at the maximum of the kinetic curve at 634 nm (Fig. 4c) may be expressed by the relation

$$v_{\max} = k_4[\mathrm{CoTSP}][\mathrm{O_2}] - k_{-4}[\mathrm{CoTSP.O_2}] - k_7[\mathrm{CoTSP.O_2}][\mathrm{CoTSP}] = 0 \, . \tag{4}$$

Assuming that the molar absorption coefficient of the unstable adduct is close to those of the other components, thus having a value in the range $5 \cdot 10^4 - 1 \cdot 10^5 \text{ l mol}^{-1}$. cm^{-1}, the maximum concentration of the adduct may be estimated from the height of the maximum in the kinetic curve as $5 \cdot 10^{-8} \text{ mol l}^{-1}$. There is practically no change in either the oxygen concentration or the equilibrium monomer concentration on formation of the adduct, so that the calculations can be made using values measured at the start of the reaction; since the value of the product of concentrations is of the order of 10^{-14}, the last term of Eq. (4) may be neglected. Hence, the ratio of the rate constants may be expressed as

$$k_4/k_{-4} = [\text{CoTSP.O}_2]/[\text{CoTSP}] [\text{O}_2] \approx 1 \cdot 10^2 \text{ l mol}^{-1} . \tag{5}$$

The value of the rate constant for the reaction $\text{CoTSP.O}_2 + \text{CoTSP} \rightarrow \text{CoTSP.O}_2$. .CoTSP, k_7, was determined from the slow phase of the kinetic curve recorded at 670 nm, corresponding to the formation of the stable adduct (Fig. 3a). For the initial reaction rate, it holds

$$v_7^0 = k_7[\text{CoTSP.O}_2] [\text{CoTSP}] = 3 \cdot 2 \cdot 10^{-10} \text{ mol l}^{-1} \text{ s}^{-1} , \tag{6}$$

and hence, considering the above given estimates for the concentrations, $k_7 = 4 \cdot 10^3$ $\text{l mol}^{-1} \text{ s}^{-1}$.

The rate constant k_{-7} was determined from the initial reaction rate of the decomposition of the stable adduct $\text{CoTSP.O}_2.\text{CoTSP}$ by an addition of sulphuric acid $(\lambda = 670 \text{ nm})$. The initial reaction rate is given as

$$v_{-7}^0 = k_{-7}[\text{CoTSP.O}_2.\text{CoTSP}] = 3 \cdot 3 \cdot 10^{-8} \text{ mol l}^{-1} \text{ s}^{-1} , \tag{7}$$

TABLE II
Rate constants of the reaction steps

	Rate constant
k_1	$2 \cdot 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$
k_2	$1 \cdot 1 \cdot 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$
k_4/k_{-4}	$1 \cdot 10^2 \text{ l mol}^{-1}$
k_5	$1 \cdot 23 \text{ s}^{-1}$
k_6	$3 \cdot 10^2 \text{ s}^{-1}$
k_{-6}	$6 \cdot 2 \cdot 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$
k_7	$4 \cdot 10^3 \text{ l mol}^{-1} \text{ s}^{-1}$
k_{-7}	$2 \cdot 6 \cdot 10^{-2} \text{ s}^{-1}$

and hence, since the initial concentration of the stable adduct is $1 \cdot 25 \cdot 10^{-6}$ mol . l^{-1}, $k_{-7} = 2 \cdot 6 \cdot 10^{-2}$ s^{-1}. However, this value has been obtained under conditions different from those where ascorbic acid oxidation occurs, and may therefore be expected to be somewhat higher. The values of all the constants determined are summarized in Table II.

Comparison of the results presented in this work with those obtained for the system catalyzed by vanadyl tetrasulphophthalocyanine[13] reveals several analogies. In both cases the system behaves as if the monomer-dimer pre-equilibrium is entirely mobile, though the rate constants quoted in the literature would indicate that the equilibrium cannot be sufficiently mobile. The rate constants obtained under conditions where the reaction under study occurs are by several orders of magnitude higher than the literature data. The rate constant k_2 for the reaction between the binary adduct CoTSP.A and oxygen is of the order of 10^6, thus being very probably the highest rate constant of the catalytic cycle, in analogy with the system catalyzed by VOTSP. The observation that the entry of a substrate as a ligand into the coordination sphere of the catalyzing complex affects the rate of dioxygen bonding has been reported for several systems[1,2,13], and seems to be of general importance in reactions of dioxygen proceeding by the coordination mechanism.

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