Catalyzed Autoxidation of Hydrogensulfite by Cobalt(II) (2,3,9,10-tetramethyl-1,4,8,11-tetraaza-cyclotetradeca-1,3,8,10-tetraene) (H 2 O) 2 2+

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Catalyzed Autoxidation of Hydrogensulfite by Cobalt(II) (2,3,9,10-tetramethyl-1,4,8,11-tetraaza-cyclotetradeca-1,3,8,10-tetraene)$(H_2O)_2^{2+}$

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The catalytic autoxidation of hydrogensulfite (hydrogentrioxosulfate(1-)) in the presence of Co(tim)$(H_2O)_2^{2+}$ (tim = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene) was studied. Dioxygen reacts with excess sulfite in the presence of Co(tim)$(H_2O)_2^{2+}$ in a complex process (a minimum of five kinetic steps can be identified) to produce Co(tim)$(SO_3)_x^{(3-2x)+}$ ($x = 1$ or 2) (λ_{max} at 350 nm) and sulfate. Seventy turnovers over 4 h were attained in a system where dioxygen and sulfite were supplied constantly. The Co(III) product formed reacts only slowly with dioxygen to produce sulfate. A mechanistic analysis of the results implies the involvement of a Co(tim)-dioxygen adduct, stabilized by an axial sulfite ligand.

Keywords: Cobalt complexes; Catalyzed autoxidation; Sulfite (hydrogentrioxosulfate(1-)); Dioxygen

INTRODUCTION

Co(tim)$(H_2O)_2^{2+}$ (Fig. 1, tim $= 2, 3, 9, 10$-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene) hardly reacts with dioxygen under ambient conditions. However, it was observed that Co(tim)$(H_2O)_2^{2+}$ is oxidized slowly by dioxygen in the presence of a variety of anionic axial ligands (e.g. acetate and chloride) probably via the formation of the weak complexes (tim)XCo$^{II}O_2$ [1]. In a recent study, the involvement of the 1:1 dioxygen adduct in the catalytic autoxidation of azide in the presence of Co(tim)$(H_2O)_2^{2+}$ was reported [2]. In the presence of Co(tim)$(H_2O)_2^{2+}$ dioxygen reacts with azide in a complex process to produce Co(tim)$(N_3)_x^{(3-x)+}$ ($x = 1$ or 2) (λ_{max} at 340 nm) and dinitrogen. The reaction is clearly catalytic with up to several hundred turnovers. The results, including the dioxygen dependence of the process, implied the involvement of a dioxygen adduct, stabilized by an axial azide ligand.

As a variety of cobalt complexes were studied in respect to the catalytic autoxidation of sulfur(IV)-oxides in aqueous solutions [3–5], it seemed of interest to extend our studies to the catalytic autoxidation of sulfite in the presence of Co(tim)$(H_2O)_2^{2+}$. Metal-catalyzed autoxidations of sulfur(IV) have importance in atmospheric chemistry as well as in industrial systems (flue gas desulfurization, "waterflood" process, O$_2$ degassing) [3,5]. Unless a radical mechanism is favored (outer sphere reaction), it is generally believed that the first step in the catalytic cycle is the formation of a metal-sulfito complex and that the active state of the metal is its higher oxidation state (usually 3+). The ensuing reaction steps are less well defined and several mechanistic interpretations prevail [3].

EXPERIMENTAL

Materials: All solutions were prepared from A.R. grade chemicals and from distilled water further purified by passing through a Millipore Milli Q setup, final resistivity $> 10 \, M\Omega/cm$.

The complex Co[(tim)Cl$_2$]Cl was prepared according to literature procedures [6,7] and characterized by NMR and UV–Vis spectroscopy. Solutions of Co(tim)Cl$_2^+$ at pH = 2.0 were reduced by the introduction of the Adams catalyst, PtO$_2$, and
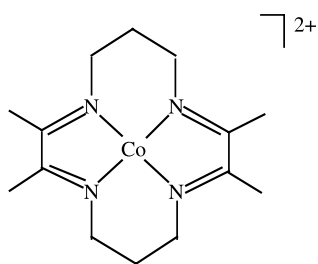
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FIGURE 1 Co(tim)$^{2+}$ (tim = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene).

bubbling dihydrogen for ca. 1 h. The spectrum of Co(tim)(H$_2$O)$_2^{2+}$ thus obtained is identical to that reported in the literature [6–8].

Techniques: Solutions were handled by the syringe technique.

The pH was measured with a HANNA HI 9017 pH meter, and was adjusted by HClO$_4$ and/or NaOH.

The kinetics of reaction of Co(tim)(H$_2$O)$_2^{2+}$ with excess sulfite in the presence of dioxygen were investigated using an Applied Photophysics SX.18MV stopped flow system. Formation and decay were followed at 260, 350 and 520 nm, respectively.

Slow follow-up reactions were studied with an HP 8452A diode array spectrophotometer. In that case, the reaction order and rate constants were evaluated with the help of the Olis kinetics fit program by On-line instrument systems.

Product analysis: The concentration of Co(tim)(H$_2$O)$_2^{2+}$ was determined spectrophotometrically using the known extinction coefficient (ε_{545} = 3450 M^{-1} cm^{-1}) [8]. The concentrations of sulfate (tetraoxosulfate(2-)) formed and sulfite remaining in the system (coordinated and free) were determined by ion chromatographic separation and elution of anions on the Hamilton-PRP-X100 separator column (250 × 4.1 mm^2) using a Jasco PU-980 Intelligent HPLC Pump and was optimized utilizing 80:20 8 mM *p*-hydroxybenzoic acid (pH 10.0):methanol eluent. The eluent flow rate was 1.5 ml/min and a suppressed conductivity detector was used. No other anions could be detected.

RESULTS

Preliminary experiments confirmed that Co(tim)(H$_2$O)$_2^{2+}$ neither reacts alone with dioxygen nor with sulfite in aqueous solutions under conditions relevant to the autoxidation studies and likewise sulfite does not react with dioxygen alone. In the presence of Co(tim)(H$_2$O)$_2^{2+}$ (0.7–3.0 × 10^{-4} M) at pH 2.5–5 dioxygen reacts with excess sulfite (1.0–3.0 × 10^{-3} M) in a complex process, consisting of a minimum of 4–5 overlaying reactions. The process can be separated into two time-scales, a fast process

lasting several 100 ms and a relatively slow process, which terminates after approximately 100 s under our experimental conditions. Figure 2 shows the spectral changes during the first phase of the reaction. During the short time-scale, the absorbance at the maximum of Co(tim)(H$_2$O)$_2^{2+}$ (545 nm) decreases, after an immediate drop in absorbance followed by an increase in the first couple of ms, close to the dead time of the stopped flow system (1.5 ms). Figure 3 shows the dioxygen dependence of this reaction followed at 520 nm. The kinetics of this decrease in absorption can be reasonably well fitted by two overlaying reactions obeying first order rate laws. During this time scale, new absorption bands with maxima around 260 and 350 nm appear (Fig. 2). The kinetics of formation of the band at 260 nm (Fig. 4) exhibits a mirror image of the reaction at 520 nm. After an initial jump in the absorbance faster than the observable time scale, the absorption decreases slightly, close to the dead time of the apparatus, followed by an increase in absorption. The values of the derived rate-constants roughly correspond to those derived at 520 nm (see Tables I–III). Figures 5 and 6 show the intricacy of the system following the reaction at 350 nm. In air-saturated solutions, the process again involves a decrease in the absorption, close to the dead time of the instrument, followed by a minimum of three reactions during the short time-scale. Figure 5 shows the sulfite dependence of this process. The dioxygen dependence of the reaction shows further complexity (Fig. 6). At 520 nm (Fig. 3), the initial-observed absorbance is lower the higher the dioxygen concentration although the first observable reaction rates are comparable for all dioxygen concentrations (0.13–1.3 × 10^{-3} M). The absorbance is lower than that calculated for the initial Co(tim)(H$_2$O)$_2^{2+}$ concentration for all cases, indicating that more Co(tim)(H$_2$O)$_2^{2+}$ reacted with dioxygen, the higher its concentration within the dead time of the instrument. At 260 nm, the initial observable absorbance increases considerably with
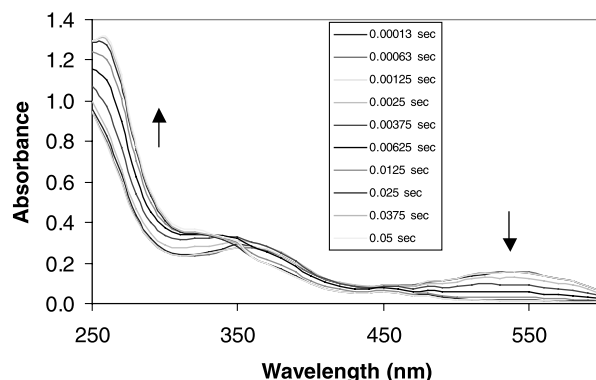

FIGURE 2 Initial spectral changes measured in a stopped flow system during the reaction of Co(tim)(H$_2$O)$_2^{2+}$ (7.5 × 10^{-5} M), HSO$_3^-$ (2.0 × 10^{-3} M), and dioxygen (1.0 × 10^{-3} M) at pH 3.0.

FIGURE 3   Dioxygen dependence of the kinetic traces (at 520 nm) measured in a stopped flow system during the reaction of $Co(tim)(H_2O)_2^{2+}$ $(7.5 \times 10^{-5}\,M)$, HSO_3^- $(2.0 \times 10^{-3}\,M)$, and dioxygen at pH 3.0.
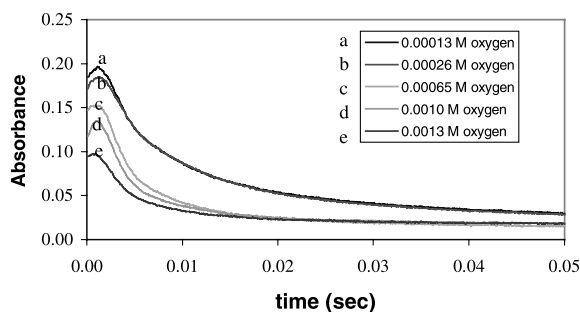

FIGURE 5   Sulfite dependence of the kinetic traces (at 350 nm) measured in a stopped flow system during the reaction of $Co(tim)(H_2O)_2^{2+}$ $(7.5 \times 10^{-5}\,M)$, dioxygen $(2.6 \times 10^{-4}\,M)$, and HSO_3^- $(1-3 \times 10^{-3}\,M)$ at pH 3.0.

increasing dioxygen concentration, indicating that more transient or product is formed initially, higher for dioxygen concentration. At 350 nm (Fig. 6), the appearance of the kinetics changes more drastically with the dioxygen concentration. It seems that mainly the second observable reaction is influenced by the dioxygen concentration. At higher dioxygen concentrations ($> 5 \times 10^{-4}\,M$), the increase in absorbance observed for lower dioxygen concentrations changes into a decrease. In Tables I–III, several selected examples of apparent rate constants are summarized for the short time-range of the process to show the general trend. It should be noted, however, that the rates are associated with a high error, due to the complexity of the system, which clearly involves more than the two processes assumed. Nonetheless one might conclude, that the rates are slightly dependent on the sulfite concentrations, but independent of Co(II), dioxygen concentration or pH in the region 2.0–4.0.

At longer time scales, a decrease in the absorbance at 260 nm mirrored by an increase at 350 nm is observed (see spectra and kinetics in Fig. 7). This reaction is comparable to that of Co(III)tim with sulfite (Fig. 8). The absorbance at 260 nm is therefore

assigned to $Co(III)(tim)(H_2O)_2^{3+}$, i.e. this is one of the final products of the fast process. Figure 9 shows the spectra of $Co(tim)(H_2O)_2^{2+}$, $Co(III)(tim)(H_2O)_2^{3+}$ and of reaction mixtures for comparison. Final products of the reaction are $Co(tim)(SO_3)_x(H_2O)_{2-x}^{(3-x)+}$ ($x = 1$ or 2) (λ_{max} at 350 nm) and sulfate. The cobalt product was identified by comparing the spectrum of the product of the reaction of $Co(tim)(H_2O)_2^{3+}$ with sulfite (Figs. 8 and 9) in He-saturated solutions to that of the Co(II)(tim)/O_2/sulfite system. The ligand-exchange reaction proceeds on the same time scale as the slow phase of the catalytic reaction. The resulting spectrum is similar to that of $trans-Co(NH_3)_4(SO_3 - \kappa S)_2^-$, λ_{max} (nm) $(\varepsilon_{max}(M^{-1}\,cm^{-1})) = 327(29500)$, 430sh(490) and less so to that of $trans-Co(NH_3)_4(H_2O)(SO_3-\kappa S)^+$, $\lambda_{max}(\varepsilon_{max}) = 273(6460)$, 473(120) [9]. One can calculate a lower limit for the extinction coefficient of $Co(tim)(SO_3)_x(H_2O)_{2-x}^{(3-x)+}$ at 350 nm as 20,000 $M^{-1}\,cm^{-1}$ from Fig. 7, assuming that all Co(II)tim is eventually transformed into the Co(III) sulfite product. Thus, it is reasonable to conclude that the final product contains two κS-sulfite ligands in trans positions. The apparent formation constant of $Co(III)tim(H_2O)(SO_3)^+$ was determined as $950 \pm 50\,M^{-1}$ at pH = 3.0 by spectrophotometric
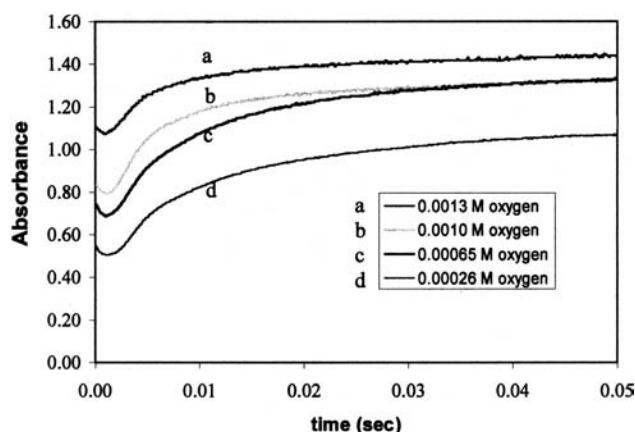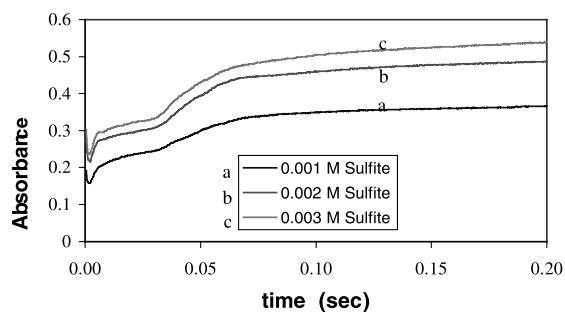

FIGURE 4   Dioxygen dependence of the kinetic traces (at 260 nm) measured in a stopped flow system during the reaction of $Co(tim)(H_2O)_2^{2+}$ $(7.5 \times 10^{-5}\,M)$, HSO_3^- $(2.0 \times 10^{-3}\,M)$, and dioxygen at pH 3.0.

TABLE I   Reaction of sulfite and dioxygen in the presence of Co(tim)(H$_2$O)$_2^{2+}$ (during the fast time-scale), followed at pH = 3.0 (rates of the faster and slower reactions). At 260 and 520 nm, the reactions were fitted to a double exponential equation (excluding the initial absorbance changes close to the dead time of the instrument. At 350 nm, the reactions were divided into two parts. The first part until the distinctive break was fitted to a double exponential equation, while the second part was fitted to a single exponential expression

			$k_{obs} \times 10^{-2}$ (s^{-1})			
λ	[O$_2$]	[Co(tim)$^{2+}$] $\times 10^4$ M	1.0×10^{-3} [HSO$_3^-$]	1.5×10^{-3} [HSO$_3^-$]	2.0×10^{-3} [HSO$_3^-$]	3.0×10^{-3} [HSO$_3^-$]
520	2.6×10^{-4}	0.75	0.99 (0.17)	1.70 (0.32)	2.52 (0.57)	3.00 (0.54)
520	2.6×10^{-4}	1.12	1.19 (0.28)	2.03 (0.35)	2.62 (0.45)	3.14 (0.46)
520	2.6×10^{-4}	1.50	1.98 (0.41)	2.47 (0.46)	2.81 (0.48)	3.68 (0.55)
520	2.6×10^{-4}	3.00	1.33 (0.17)	2.17 (0.33)	3.22 (0.42)	4.37 (0.60)
260	2.6×10^{-4}	0.75	0.85 (0.20)	1.50 (0.30)	2.49 (0.50)	3.46 (0.51)
260	2.6×10^{-4}	1.12	0.99 (0.23)	2.05 (0.38)	2.53 (0.52)	2.88 (0.52)
260	2.6×10^{-4}	1.50	1.83 (0.37)	2.32 (0.42)	2.84 (0.53)	3.55 (0.60)
350	2.6×10^{-4}	0.75	1.74 (1.1) (0.20)	1.6 (0.8) (0.31)	2.66 (0.57) (0.35)	3.48 (0.67) (0.50)
350	2.6×10^{-4}	1.12	1.74 (1.2) (0.38)	2.4 (1.1) (0.60)	2.61 (0.78) (0.53)	3.36 (0.72) (0.43)
350	2.6×10^{-4}	1.50	2.41 (1.23) (0.41)	2.5 (0.82) (0.50)	2.67 (0.72) (0.49)	3.78 (1.20) (0.49)
350	2.6×10^{-4}	3.00	2.37 (0.85) (0.26)	2.62 (0.90) (0.46)	3.55 (0.91) (0.46)	3.82 (0.88) (0.53)

k_{obs} = observed rate constants.

determination at the completion of the reaction in a system containing Co(III)(tim)(H$_2$O)$_2^{3+}$ (1×10^{-3} M) and sulfite ($1.0-4.0 \times 10^{-4}$ M). These results point out that Co(III)(tim)(H$_2$O)$_2^{3+}$ does not oxidize sulfite.

Sulfate is the only oxidation product of sulfite in this system. The SO$_4^{2-}$ yields are summed up in Table IV. Under conditions of high dioxygen concentration about 2/3–3/4 of the initial sulfite is converted into sulfate, while unreacted sulfite remains in the system. At high sulfite concentrations, the sulfate yield approaches twice the O$_2$ concentration. With less dioxygen (air saturated solutions), the yield of sulfate is slightly higher than twice the dioxygen. As the maximal yield of sulfate is expected to be twice the dioxygen concentration, which corresponds to the stoichiometric conversion of sulfite to sulfate, it should be noted, that while these reactions were performed avoiding additional inlet of air as much as possible, some air entry during the injection into the ion chromatograph could not be avoided. Samples, which were left open to air, produced considerably higher sulfate amounts than those tabulated. High dioxygen concentrations are needed for efficient catalysis. When the reaction was performed under constant dioxygen flow and

addition of sulfite (dioxygen was bubbled through a trap containing sulfite at pH = 3), the catalytic turnover could be increased and approached ca. 70 turnovers over 4 h in one trial run.

DISCUSSION

The transition metal-catalyzed oxidation of sulfur(IV) oxides is extensively reviewed in a recent article by van Eldik *et al.* [3]. A wealth of reactions is possible in such systems and the reader is referred to that review for details. Topics relevant to this work are highlighted in the following.

Nonradical mechanisms, radical, and a combination of radical and nonradical mechanisms are discussed in the literature for the transition metal-catalyzed oxidation of sulfur(IV) oxides by dioxygen. The nonradical mechanism is presumably initiated by an inner sphere complexation of the sulfite and possibly dioxygen (in the presence of dioxygen), followed by electron transfer. Different metal-sulfito complexes may be formed (co-ordination number, co-ordination via S or O, SO$_3^{2-}$, HSO$_3^-$ co-ordination, etc.) [3].

TABLE II   Reaction of sulfite and dioxygen in the presence of Co(tim)(H$_2$O)$_2^{2+}$ (during the fast time-scale) at different pHs (rates of the faster and slower reactions). At 260 and 520 nm the reactions were fitted to a double exponential equation (excluding the initial absorbance changes close to the dead time of the instrument. At 350 nm, the reactions were divided into two parts. The first part until the distinctive break was fitted to a double exponential equation, while the second part was fitted to a single exponential expression

				$k_{obs} \times 10^{-2}$ (s^{-1})			
λ	pH	[O$_2$] (M)	[Co(tim)$^{2+}$] (M)	1.0×10^{-3} [HSO$_3^-$]	1.5×10^{-3} [HSO$_3^-$]	2.0×10^{-3} [HSO$_3^-$]	3.0×10^{-3} [HSO$_3^-$]
520	2.5	$2.6 \times 10 - 4$	7.5×10^{-4}	0.78 (0.22)	2.12 (0.59)	2.24 (0.33)	
260	2.5	$2.6 \times 10 - 4$	7.5×10^{-4}	0.5 (0.16)	2.14 (0.46)	2.75 (0.37)	
350	2.5	$2.6 \times 10 - 4$	7.5×10^{-4}	0.95 (0.16)	4.04 (0.46)	5.10 (0.21)	
520	3.0	$2.6 \times 10 - 4$	7.5×10^{-4}	0.99 (0.17)	1.7 (0.32)	2.52 (0.57)	3.00 (0.54)
260	3.0	$2.6 \times 10 - 4$	7.5×10^{-4}	0.85 (0.20)	1.50 (0.30)	2.49 (0.50)	3.46 (0.51)
350	3.0	$2.6 \times 10 - 4$	7.5×10^{-4}	1.74 (1.1) (0.20)	1.6 (0.8) (0.31)	2.66 (0.57) (0.35)	3.48 (0.67) (0.50)

k_{obs} = observed rate constants.

TABLE III   Reaction of sulfite (2.0×10^{-3} M) and dioxygen in the presence of Co(tim)(H$_2$O)$_2^{2+}$ (during the fast time scale) at different [O$_2$]

| λ	[O$_2$]	[Co(tim)$^{2+}$] $\times 10^4$ M	$k_{obs} \times 10^{-2}$ (s^{-1})		
			k_1	k_2	k_3
520	1.3×10^{-4}	0.75	3.12	0.61	
520	2.6×10^{-4}	0.75	2.51	0.57	
520	6.5×10^{-4}	0.75	3.64	0.72	
520	9.75×10^{-4}	0.75	4.45	0.85	
520	1.3×10^{-3}	0.75	4.07	0.79	
260	1.3×10^{-4}	0.75	3.32	0.59	
260	2.6×10^{-4}	0.75	2.48	0.50	
260	6.5×10^{-4}	0.75	3.13	0.40	
260	9.75×10^{-4}	0.75	4.89	0.35	
260	1.3×10^{-3}	0.75	3.10	0.38	
350	1.3×10^{-4}	0.75	3.24	(formation)	0.47
350	2.6×10^{-4}	0.75	2.66	0.57 (formation)	0.35
350	6.5×10^{-4}	0.75	3.70	1.39 (decay)	0.50
350	9.75×10^{-4}	0.75	5.20	1.74 (decay)	0.27
350	1.3×10^{-3}	0.75	3.63	2.02 (decay)	0.57

k_{obs} = observed rate constants.

The radical mechanism on the other hand is proposed to commence with an outer sphere electron transfer reaction between metal complex and sulfite:

$$M^{n+} + HSO_3^- \leftrightarrows M^{(n-1)+} + SO_3^{\cdot-} + H^+$$

followed by a range of possible radical processes [3]. In the absence of dioxygen, SO$_3^{\cdot-}$ reacts further mainly via the following reactions:

$$M^{n+} + SO_3^{\cdot-} \leftrightarrows M^{(n-1)+} + SO_4^{2-} + 2H^+$$

$$SO_3^{\cdot-} + SO_3^{\cdot-} \rightarrow S_2O_6^{2-}$$
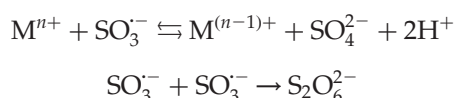
In the presence of dioxygen, the SO$_3^{\cdot-}$ radicals react primarily via:

$$SO_3^{\cdot-} + O_2 \leftrightarrows SO_5^{\cdot-}$$
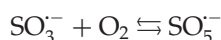
The reaction of SO$_3^{\cdot-}$ with dioxygen is very fast ($k = 1-2 \times 10^9$ M^{-1} s^{-1}) [3] and competes with the reoxidation of the reduced-metal species by the sulfite radical. The SO$_5^{\cdot-}$ radical is a strong oxidant and can undergo a series of reactions eventually generating primarily SO$_4^{2-}$. Via radical–radical reactions S$_2$O$_6^{2-}$ is produced, e.g.:
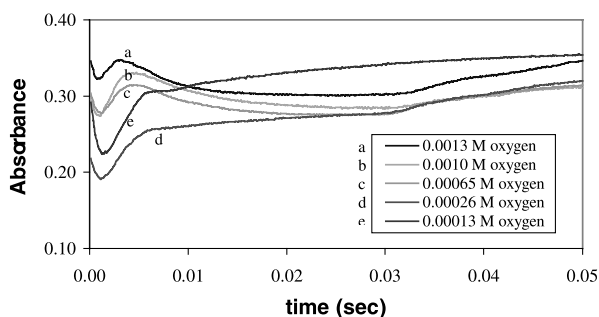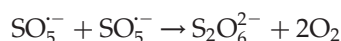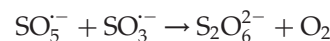
$$SO_5^{\cdot-} + SO_5^{\cdot-} \rightarrow S_2O_6^{2-} + 2O_2$$

FIGURE 6   Dioxygen dependence of the kinetic traces (at 350 nm) measured in a stopped flow system during the reaction of Co(tim)(H$_2$O)$_2^{2+}$ (7.5×10^{-5} M), HSO$_3^-$ (2.0×10^{-3} M), and dioxygen at pH 3.0.

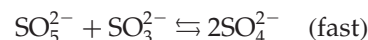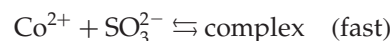$$SO_5^{\cdot-} + SO_3^{\cdot-} \rightarrow S_2O_6^{2-} + O_2$$

Moreover, the SO$_5^{\cdot-}$ radical is probably the main species to reoxidize the reduced transition-metal species [3,10–12].

In order for a cobalt(II) complex to exhibit catalytic activity, it presumably has to be transformed initially into a higher valence state. An induction period is, therefore, generally observed. Hobson *et al.* [5] suggested the following initiation sequence:

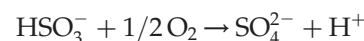$$Co^{2+} + SO_3^{2-} \overset{slow}{\leftrightarrows} CoSO_3 \overset{+O_2}{\rightarrow} O_2CoSO_3$$

The oxidation of sulfur(IV) was only observed as long as dioxygen was still present in such a system.

The cobalt(II)-catalyzed autoxidation of sulfur species in the presence of dioxygen was schematically proposed to occur via [3]:

$$Co^{2+} + SO_3^{2-} \leftrightarrows complex \quad (fast)$$

$$complex + O_2 \leftrightarrows SO_5^{2-} + Co^{2+} \quad (slow)$$

$$SO_5^{2-} + SO_3^{2-} \leftrightarrows 2SO_4^{2-} \quad (fast)$$

with the overall stoichiometry of:

$$HSO_3^- + 1/2\,O_2 \rightarrow SO_4^{2-} + H^+$$

In this work, the catalytic autoxidation of sulfite by dioxygen in the presence of Co(tim)(H$_2$O)$_2^{2+}$ was studied. Co(tim)(H$_2$O)$_2^{2+}$ possesses a very low affinity for dioxygen (there is no direct evidence for the formation of a dioxygen adduct, but K was estimated at 1 M^{-1}) [13,14] and is only very slowly oxidized by O$_2$ at room temperature. Addition of chloride or bromide [8], which serve as axial bases, is needed to efficiently oxidize Co(tim)$^{2+}$ to Co(tim)$^{3+}$, probably via the formation of the weak complex (tim)XCo^{III}(O$_2^-$). In a recent study, the involvement of the 1:1 dioxygen adduct in the catalytic autoxidation

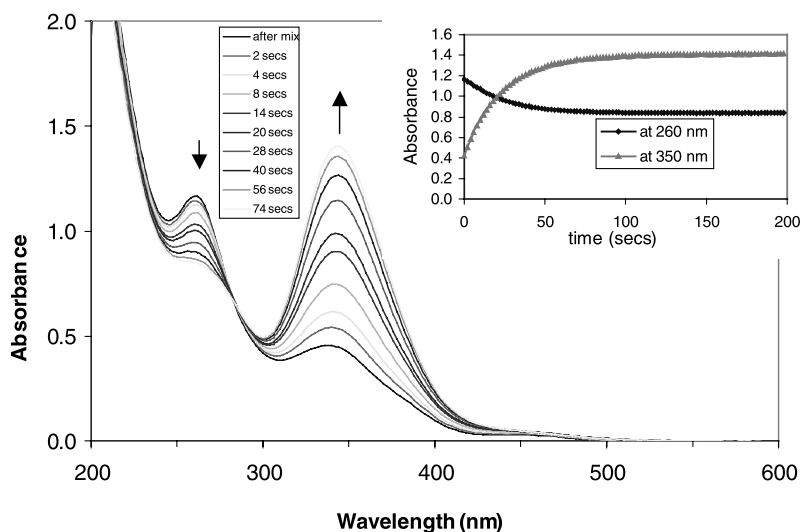FIGURE 7   Slow UV–Vis spectral changes during the reaction of $Co(tim)(H_2O)_2^{2+}$ (7.5×10^{-5} M), dioxygen (2.6×10^{-4} M), and HSO_3^- (1.0×10^{-3} M) at pH 3.0. Inset: kinetic traces at 260 and 350 nm.

of azide in the presence of $Co(tim)(H_2O)_2^{2+}$ was conveyed [2]. In analogy to the azide system and in accord with the mechanism suggested by Hobson [5], it is proposed that the initial stage of the catalytic cycle involves the formation of a Cobaltsulfito-dioxygen complex, probably $trans-(tim)Co^{III}(SO_3^{2-} - \kappa S)(O_2^{.-})$. This complex has probably a considerable absorption coefficient at 260 nm and its formation thus explains the initial very fast increase in absorption at 260 nm (concomitant with a decrease in absorption at 520 nm) within the dead time of the stopped flow instrument. Following this reaction, one can observe a series of reaction steps (see figures and tables), showing the intricacy of the catalytic system. As the optical changes observed are due to the disappearance of $Co(tim)(H_2O)_2^{2+}$ and the formation of $Co(tim)(H_2O)_2^{3+}$ and $Co(tim)-(SO_3^- \kappa S)_x(H_2O)_{2-x}^{(3-2x)+}$, i.e. to termination reactions and not to the formation of SO_4^{2-}, one should not

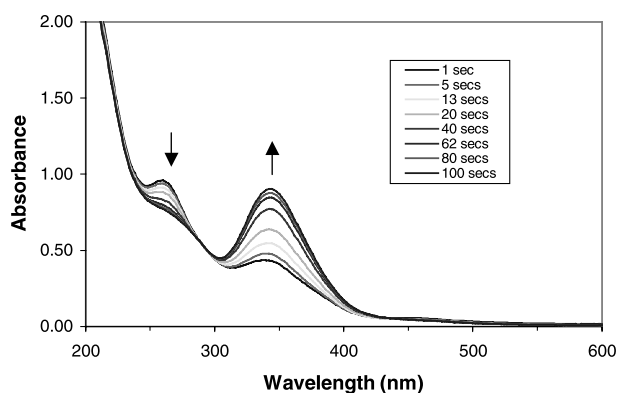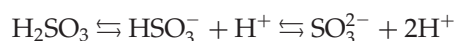expect straightforward kinetic relationships, as the observed processes are those connected with the termination of the reaction.

During the faster time scale, the conversion of $Co(tim)(H_2O)_2^{2+}$ (decrease of absorption at 520 nm) into $Co(tim)(H_2O)_2^{3+}$ (increase of absorption at 260 nm) is observed. The immediate decay at 520 nm and increase in absorption at 260 nm within the dead time of the instrument are attributed, as explained above, to the formation of the $[(SO_3^{2-}) - Co^{III}(tim) - O_2^{.-}]$ complex, the "active" species. The rather complex behavior of the kinetics at 350 nm seems to be an indication that several termination reactions occur and that their relative contributions depend on the concentrations of the different participants in the catalytic process.

The reaction during the seconds time scale is assigned to the ligand-exchange reaction of $Co(tim)(H_2O)_2^{3+}$ (260 nm product) with sulfite to produce $Co(tim)(SO_3 - \kappa S)_x(H_2O)_{2-x}^{(3-2x)+}$ ($x = 1$ or 2) (λ_{max} at 350 nm). $Co(tim)(H_2O)_2^{2+}$ is no longer detectable in the system at that time. It should be noted here that the formation of the Cobalt(III) sulfite complex is a rather slow process under our experimental conditions, opposed to the proposed fast formation of such complexes in many catalytic systems [3]. The only product based on sulfite produced in the studied system is sulfate and it is produced at roughly twice the initial dioxygen concentration.

In accord with the above observations, it is proposed that the following reactions are the major partaking in the mechanism.

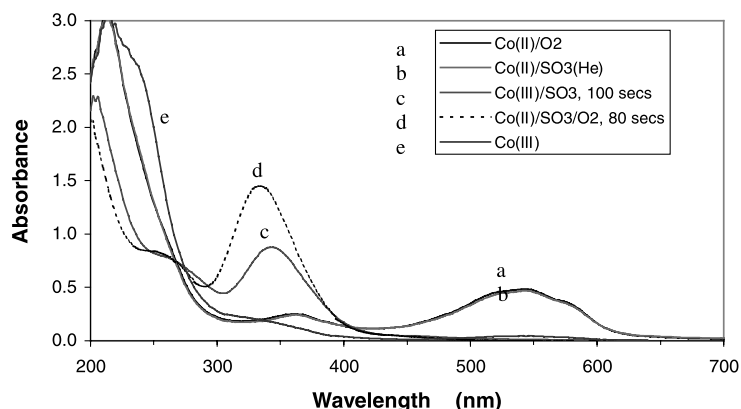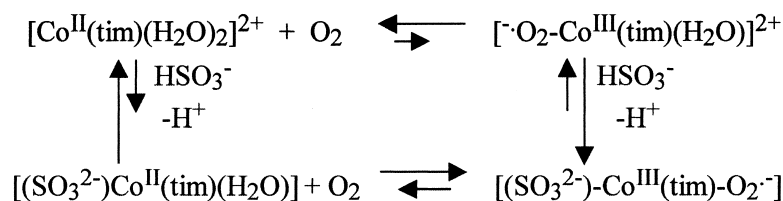FIGURE 8   Slow UV–Vis spectral changes during the reaction of $Co(tim)(H_2O)_2^{3+}$ (5.0×10^{-5} M), and HSO_3^- (5.0×10^{-4} M) at pH 3.0.

$$H_2SO_3 \leftrightarrows HSO_3^- + H^+ \leftrightarrows SO_3^{2-} + 2H^+$$

$$pKa = 1.86/7.2$$

FIGURE 9   UV–Vis spectra of (a) $Co(tim)(H_2O)_2^{2+}$ (1.3×10^{-4} M), dioxygen (2.6×10^{-4} M). (b) $Co(tim)(H_2O)_2^{2+}$ (1.3×10^{-4} M), HSO_3^- (1.0×10^{-3} M). (c) $Co(tim)(H_2O)_2^{3+}$ (5.0×10^{-5} M), and HSO_3^- (5.0×10^{-4} M) under He after 100 s. (d) $Co(tim)(H_2O)_2^{2+}$ (7.5×10^{-5} M), dioxygen (2.6×10^{-4} M) and HSO_3^- (1.0×10^{-3} M) after 80 s. (e) $Co(tim)(H_2O)_2^{3+}$ (1.0×10^{-4} M) under He.
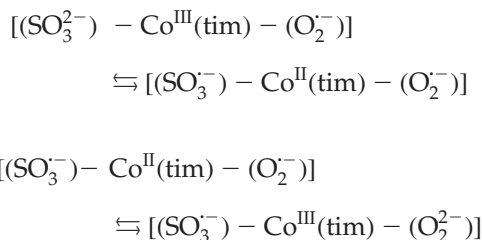
(See Refs. [15,16]) HSO_3^- is the dominant species in the region of $2.0 < pH < 6.0$. HSO_3^- or SO_3^{2-} might be coordinated to any Cobalt complex in the following reactions. For simplicity, only SO_3^{2-} is used as a ligand. The initial formation of a reactive Cobalt-sulfito-oxygen complex is proposed.
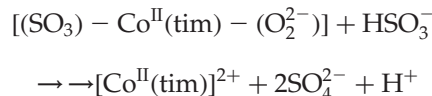
$$[(SO_3^{\cdot-}) - Co^{III}(tim) - (O_2^{2-})]$$

$$\leftrightarrows [(SO_3) - Co^{II}(tim) - (O_2^{2-})]$$
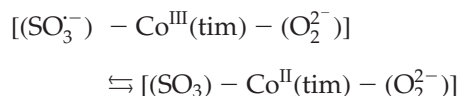
Cobalt(II) is probably returned to the catalytic cycle

$$[Co^{II}(tim)(H_2O)_2]^{2+} + O_2 \leftrightarrows [^{\cdot}O_2\text{-}Co^{III}(tim)(H_2O)]^{2+}$$

$$\updownarrow \, HSO_3^- \quad\quad\quad \updownarrow \, HSO_3^-$$
$$-H^+ \quad\quad\quad\quad -H^+$$

$$[(SO_3^{2-})Co^{II}(tim)(H_2O)] + O_2 \leftrightarrows [(SO_3^{2-})\text{-}Co^{III}(tim)\text{-}O_2^{\cdot-}]$$

This complex is probably present as a mixture of the following forms:

$$[(SO_3^{2-}) - Co^{III}(tim) - (O_2^{\cdot-})]$$

$$\leftrightarrows [(SO_3^{\cdot-}) - Co^{II}(tim) - (O_2^{\cdot-})]$$

$$[(SO_3^{\cdot-}) - Co^{II}(tim) - (O_2^{\cdot-})]$$

$$\leftrightarrows [(SO_3^{\cdot-}) - Co^{III}(tim) - (O_2^{2-})]$$

by reaction of the dioxygen-complex with additional sulfite:

$$[(SO_3) - Co^{II}(tim) - (O_2^{2-})] + HSO_3^-$$

$$\rightarrow \rightarrow [Co^{II}(tim)]^{2+} + 2SO_4^{2-} + H^+$$

or via:

$$[(SO_3) - Co^{II}(tim) - (O_2^{2-})] \xrightarrow{H_2O} [(H_2O)Co^{II}(tim)$$

$$- (O_2^{2-})] + SO_4^{2-} + 2H^+$$
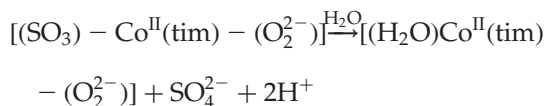
TABLE IV   Sulfate yields under different conditions

pH	$[O_2]_0$ (M)	$[Co(tim)(H_2O)_2^{2+}]_0 \times 10^4$ (M)	$[HSO_3^-]_0 \times 10^3$ (M)	$[SO_4^{2-}] \times 10^3$ (M)
3.0	1.3×10^{-3}	1.0	1.0	0.75
3.0	1.3×10^{-3}	1.0	1.5	0.98
3.0	1.3×10^{-3}	1.0	2.0	1.40
3.0	1.3×10^{-3}	1.0	3.0	2.40
3.0	constant supply	1.0	10.0	7.0 (4 h)
3.0	2.6×10^{-4}	3.0	1.0	0.46
3.0	2.6×10^{-4}	3.0	1.5	0.65
3.0	2.6×10^{-4}	3.0	2.0	0.63
3.0	2.6×10^{-4}	3.0	3.0	0.65

The $[(H_2O)Co^{II}(tim) - (O_2^{2-})]$ or $Co^{IV}(tim)$ will then oxidize a further SO_3^{2-} or release H_2O_2 into the solution.

The reaction scheme might also include the formation of some $SO_3^{\cdot-}$ radicals, as a side reaction, followed by their reaction with dioxygen to produce $SO_5^{\cdot-}$.
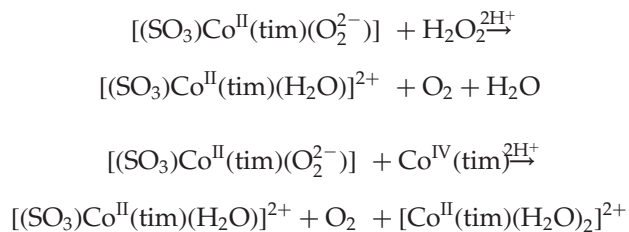
$$[(SO_3^{2-}) - Co^{III}(tim) - O_2^{\cdot-}] + HSO_3^- \rightarrow [(SO_3^{2-})$$

$$- Co^{II}(tim) - O_2^{\cdot-}] + SO_3^{\cdot-}$$

$$SO_3^{\cdot-} + O_2 \rightarrow SO_5^{\cdot-}$$

$$SO_5^{\cdot-} + [Co^{II}(tim)(H_2O)_2]^{2+}$$

$$\rightarrow [Co^{III}(tim)(H_2O)_2]^{3+} + SO_5^{2-}$$

$$SO_5^{2-} + SO_3^{2-} \rightarrow 2SO_4^{2-}$$
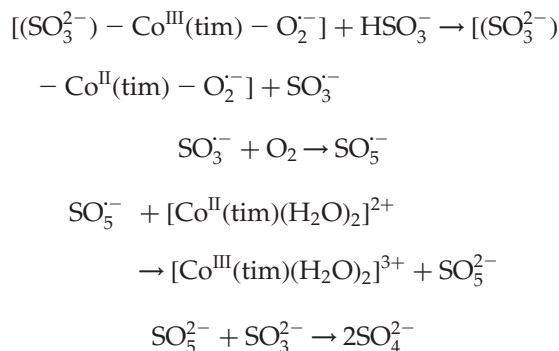
This process, which forms $[Co^{III}(tim)(H_2O)_2]^{3+}$, might be one of the termination processes. Further, termination steps of the catalytic cycle might be the following:
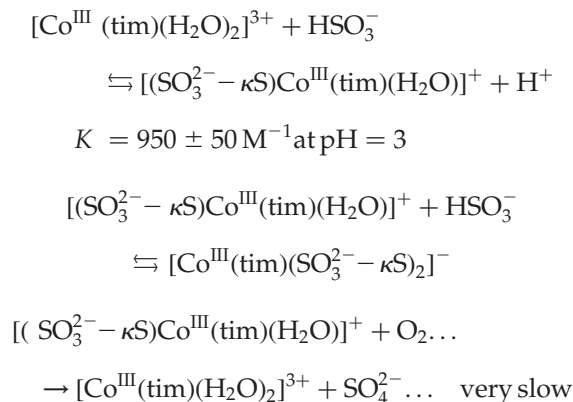
$$2[Co^{II}(tim)(H_2O)_2]^{2+} + H_2O_2 + 2H^+$$

$$\rightarrow \rightarrow 2Co^{III}(tim')^{3+} + 2H_2O \text{ termination}$$
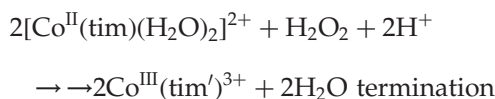
It should be noted that the reaction of H_2O_2 with Co(II)tim leads to decomposition of the tim ligand as reported by Espenson *et al.* [13].

As the termination steps are slowed down, as long as dioxygen is present, reactions of the type

$$[(SO_3)Co^{II}(tim)(O_2^{2-})] + H_2O_2 \overset{2H^+}{\rightarrow}$$

$$[(SO_3)Co^{II}(tim)(H_2O)]^{2+} + O_2 + H_2O$$

$$[(SO_3)Co^{II}(tim)(O_2^{2-})] + Co^{IV}(tim) \overset{2H^+}{\rightarrow}$$

$$[(SO_3)Co^{II}(tim)(H_2O)]^{2+} + O_2 + [Co^{II}(tim)(H_2O)_2]^{2+}$$

have to be considerably faster than the termination steps.

The "slow" reactions are:

$$[Co^{III}(tim)(H_2O)_2]^{3+} + HSO_3^-$$

$$\leftrightarrows [(SO_3^{2-} - \kappa S)Co^{III}(tim)(H_2O)]^+ + H^+$$

$$K = 950 \pm 50\,M^{-1} \text{at pH} = 3$$

$$[(SO_3^{2-} - \kappa S)Co^{III}(tim)(H_2O)]^+ + HSO_3^-$$

$$\leftrightarrows [Co^{III}(tim)(SO_3^{2-} - \kappa S)_2]^-$$

$$[(SO_3^{2-} - \kappa S)Co^{III}(tim)(H_2O)]^+ + O_2\dots$$

$$\rightarrow [Co^{III}(tim)(H_2O)_2]^{3+} + SO_4^{2-}\dots \quad \text{very slow}$$

The reaction of the complexes $[(SO_3^{2-} - \kappa S)Co^{III}(tim)(H_2O)]^+$ and $[Co^{III}(tim)(SO_3^{2-} \kappa S)_2]^-$ with dioxygen is clearly very slow.

CONCLUDING REMARKS

This study clearly demonstrates that the active intermediate in the catalytic autoxidation of HSO_3^- in the presence of $[Co^{II}(tim)(H_2O)_2]^{2+}$ is $[(SO_3^{2-})Co^{III}(tim)(O_2^{\cdot-})]$. This finding is in accord with the analogous study in the catalytic oxidation of N_3^- by the same complex [2] and the autoxidation of $[Co^{II}(tim)(H_2O)_2]^{2+}$ in the presence of Cl^-, Br^-, $CH_3CO_2^-$, etc. [1]. The results thus imply that in all these systems a transient species of the type $[(X)Co^{III}(tim)(O_2^{\cdot-})]$ is formed. The fate of this species depends on the nature of X:

1. If X can be oxidized via a two electron process, e.g. for $X = SO_3^{2-}$, then the major reactions occurring do not involve the formation of radicals.
2. If X can be oxidized by dioxygen only in a single electron process, then the follow-up reactions involve either the formation of radicals or the reaction of another X with the active transient, e.g. for $X = N_3^-$.
3. If X cannot be oxidized by dioxygen under these conditions, then only autoxidation of the $[Co^{II}(tim)(H_2O)_2]^{2+}$ is observed.

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