compounds II-P and III and the $[\mathrm{Mo(CO)_3Fe_3S_4(SR)_3}]^{3-}$ cubane,[22] all of which contain CO ligands to Mo). Since there is no evidence for the presence of either π-acid or terminal oxide or sulfide ligands on Mo in FeMo-co, the above considerations suggest that the Mo site of FeMo-co may well prove to be formally nine-coordinate when its structure is finally determined.

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Supplementary Material Available: Tables of positional and thermal parameters and bond lengths and angles for $(\mathrm{Ph_4As})_2(\mathrm{I})$, $(\mathrm{Et_4N})_2(\mathrm{I})$, $(\mathrm{Ph_4As})_2(\mathrm{II\text{-}P})$, and $(\mathrm{Ph_4As})_2(\mathrm{III})$ (38 pages); tables of observed and calculated structure factors for $(\mathrm{Ph_4As})_2(\mathrm{I})$, $(\mathrm{Et_4N})_2(\mathrm{I})$, $(\mathrm{Ph_4As})_2(\mathrm{II\text{-}P})$, and $(\mathrm{Ph_4As})_2(\mathrm{III})$ (102 pages). Ordering information is given on any current masthead page.

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Kinetics and Mechanism of the Sulfite-Induced Autoxidation of Cobalt(II) in Aqueous Azide Medium

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The autoxidation of Co(II) in azide medium is accelerated by sulfur(IV) oxides at a concentration level of 10^{-5} M. The formation of Co(III) was followed spectrophotometrically under the following conditions: $[\mathrm{Co(II)}] = 5 \times 10^{-4}$ M; initial $[\mathrm{Co(III)}] = (0\text{–}3.6) \times 10^{-5}$ M; $[\text{total S(IV)}] = (1\text{–}4) \times 10^{-5}$ M; $4 < \mathrm{pH} < 6$; $[\text{total } \mathrm{N_3^-}] = 0.1\text{–}0.5$ M; temperature = 25 °C; ionic strength = 1.0 M. The autoxidation reaction exhibits typical autocatalytic behavior in which the induction period depends on the Co(III) concentration. A detailed kinetic study of both the autoxidation step and the reduction of Co(III) by sulfur(IV) oxides demonstrates that the same rate-determining step is operative in both cases. This step involves the reduction of Co(III) by sulfur(IV) oxide to produce the $\mathrm{SO_3^-}$ radical, which reacts with dissolved oxygen to produce $\mathrm{SO_5^-}$ and rapidly oxidizes Co(II) in at least two consecutive steps. The observed rate constant depends on the pH and azide concentration, since these control the speciation of the sulfur(IV) oxides and cobalt(II/III) azide complexes. The proposed mechanism is discussed in reference to available literature information.

Introduction

We are in general interested in the metal-catalyzed autoxidation mechanism of sulfur(IV) oxides and its role in atmospheric oxidation processes, i.e. the formation of acid rain. We have in the past undertaken a detailed study of the Fe(III)-catalyzed autoxidation reactions[2-4] and are presently investigating the catalytic role of some model Fe(III) complexes.[5] A crucial step in the overall oxidation mechanism[4] concerns the oxidation of Fe(II) that is produced during the oxidation of sulfur(IV) oxides by Fe(III). Such oxidation reactions are usually slow, but it has been suggested[6] and recently found in our laboratories[7] that the autoxidation of Fe(II) is catalyzed by sulfur(IV) oxides. In this respect it should be noted that evidence for the formation of a strong oxidant (most likely $\mathrm{SO_5^{2-}}$ and $\mathrm{HSO_5^-}$) in the reaction of $\mathrm{SO_3^{2-}}$ with $\mathrm{O_2}$ has been reported.[8] This oxidant plays an important role in mineral extraction processes.

In the present study we have investigated the kinetics and mechanism of the sulfite-catalyzed autoxidation of Co(II) in the presence of azide. It is generally known that cobalt(II) azide complexes are oxidized slowly by dissolved oxygen to the corresponding Co(III) complexes. However, this reaction is markedly accelerated by sulfur(IV) oxides ($\mathrm{SO_2}$, $\mathrm{HSO_3^-}$, $\mathrm{SO_3^{2-}}$), such that it can be employed as a spot test for sulfite[9,10] and as a quantitative analytical method.[11] Preliminary measurements demonstrated that the S(IV)-catalyzed autoxidation reaction exhibits typical autocatalytic behavior that depends on the presence of Co(III) species.[11,12] It was therefore the major objective of this study to resolve the underlying reaction mechanism and so contribute toward the understanding of the catalyzed autoxidation process. At the same time we are convinced that similar reactions occur in the sulfite-catalyzed autoxidation of Fe(II) mentioned above.[7]

Experimental Section

All reagents were of analytical reagent grade (Merck), and deionized water was used to prepare all solutions. $\mathrm{N_2}$ was used to deaerate solutions where required. Stock solutions of sulfite were prepared by dissolving $\mathrm{Na_2S_2O_5}$ in deaerated water and kept in a refrigerator at 5 °C ($\mathrm{S_2O_5^{2-}}$ dissociates in water to $\mathrm{HSO_3^-}$; see ref 2). Other stock solutions were prepared by using $\mathrm{NaN_3}$, $\mathrm{HClO_4}$ (to adjust the pH), $\mathrm{NaClO_4}$ (to adjust the ionic strength to 1.0 M), and $\mathrm{Co(ClO_4)_2}$. $\mathrm{Na_3[Co(CO_3)_3]\cdot 3H_2O}$ was prepared as described in the literature[13] and used as source of Co(III). When this complex is dissolved in acidic azide buffer medium under the selected experimental conditions, it rapidly aquates via decarboxylation to produce the cobalt(III) azide complex.

UV–vis spectra were recorded on a Shimadzu UV 250 spectrophotometer, which was also used for kinetic measurements in its thermo-

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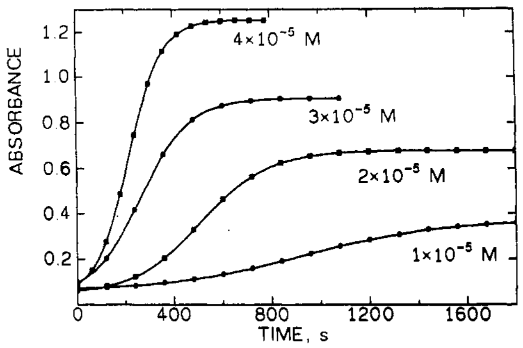

Figure 1. Absorbance at 367 nm as a function of time during the addition of sulfite to a cobalt(II) azide solution. Conditions: [Co(II)] = 5 × 10^{-4} M; [N_3^-] = 0.5 M; [O_2] = 2 × 10^{-4} M; [HN_3] = 0.1 M; pH = 5.2; ionic strength = 1.0 M; temperature = 25 °C; optical path length = 0.88 cm. [S(IV)] is indicated for each plot.

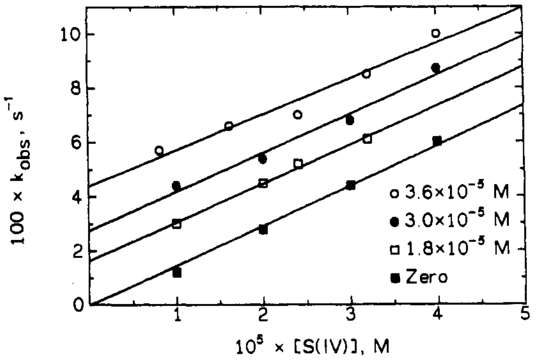

Figure 2. k_{obs} as a function of [S(IV)] for the oxidation of Co(II) in the presence of added Co(III). Conditions: [Co(II)] = 5 × 10^{-4} M; [N_3^-] = 0.1 M; [HN_3] = 0.02 M; pH = 5.0; ionic strength = 1.0 M; [O_2] = 2 × 10^{-4} M; temperature 25 °C. $[Co(III)]_i$ is indicated for each line.

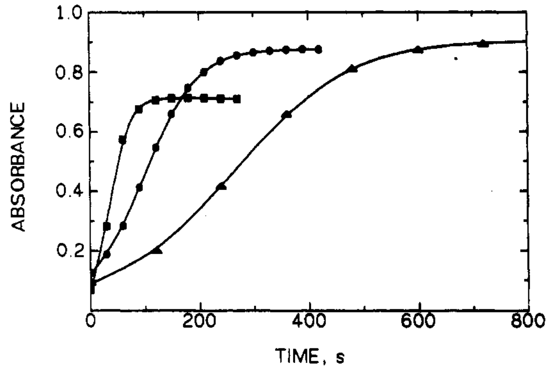

Figure 3. Absorbance at 367 nm as a function of time during the oxidation of Co(II) at various azide concentrations. Conditions: [Co(II)] = 5 × 10^{-4} M; [N_3^-]/[HN_3] = 5; pH = 5.0; [N_3^-] = 0.10 (■), 0.30 (●), 0.50 M (▲); ionic strength = 1.0 M; temperature = 25 °C; optical path length = 0.88 cm; [S(IV)] = 3 × 10^{-5} M; [O_2] = 2 × 10^{-4} M.

stated (±0.1 °C) cell compartment. For more rapid reactions, a Durrum D110 stopped-flow instrument equipped with an online data acquisition system[14] was employed. pH measurements were performed on a Metrohm 632 pH meter equipped with a Sigma glass electrode. The concentration of dissolved oxygen was monitored with a WTW OXI 91 oxygen detector. In many experiments air- and oxygen-saturated solutions were employed for which the oxygen concentration was found to be 2 × 10^{-4} and 8 × 10^{-4} M, respectively, under the selected conditions at 1.0 M ionic strength. Some further experimental details are included where appropriate in the following section.

Results and Discussion

Formation Kinetics of Cobalt(III) Azide Complexes. Solutions of Co(II) in azide (N_3^-/HN_3) medium show a very slow spontaneous oxidation by dissolved oxygen to Co(III). A detailed study of the complex formation equilibria[15,16] resulted in the overall stability constants (at 25 °C and 2 M ionic strength) β_1 = 5.7 M^{-1}, β_2 = 19 M^{-2}, β_3 = 7 M^{-3}, β_4 = 16 M^{-4}, and β_5 = 4.4 M^{-5} for the formation of complexes of the type $Co^{II}(N_3^-)_x$ compared to values of β_1 = 3 × 10^8 M^{-1}, β_2 = 1 × 10^{15} M^{-2}, β_3 = 7 × 10^{19} M^{-3}, β_4 = 1.5 × 10^{23} M^{-4}, β_5 = 1.3 × 10^{23} M^{-5}, and β_6 = 1.0 × 10^{24} M^{-6} for the formation of complexes of the type $Co^{III}(N_3^-)_x$. These formation constants indicate that the Co(III) complexes are significantly more stable than the corresponding Co(II) complexes and tend to produce species of higher coordination number with respect to azide at a particular azide concentration. Furthermore, it can be estimated that in the case of Co(II) at 0.1 M N_3^- 50% of the Co(II) is not complexed, 35% exists as $Co^{II}(N_3^-)$, and 15% exists as $Co^{II}(N_3^-)_2$ compared to 30% as $Co^{II}(N_3^-)_2$, 15% as $Co^{II}(N_3^-)_3$, and 30% as $Co^{II}(N_3^-)_4$ at 1 M N_3^-. Under the same conditions the distribution of the cobalt(III) azide complexes indicates the formation of mainly $Co^{III}(N_3^-)_4$ and $Co^{III}(N_3^-)_6$ at 0.1 and 1 M N_3^-, respectively.[16] The cobalt(III) azide complexes exhibit an intense absorption band at 365 nm (ϵ = 2.2 × 10^4 M^{-1} cm^{-1}) for azide concentrations between 0.1 and 0.5 M.

Addition of sulfite to solutions of Co(II) in azide medium in the presence of dissolved oxygen results in the rapid formation of cobalt(III) azide complexes for which the approximate overall reaction is given in (1).[11,12] This reaction suggests a formation

$$2Co(N_3)_2 + O_2 + SO_3^{2-} + 2HN_3 + 2N_3^- \rightarrow 2Co(N_3)_4^- + SO_4^{2-} + H_2O \quad (1)$$

ratio of 2:1 for the production of Co(III) compared to sulfite used. As will be seen later, this ratio is significantly smaller due to the interference of side reactions. Some typical absorbance/time traces are reported in Figure 1. In these experiments an equal volume of a sulfite solution was mixed with a solution containing Co(II), N_3^-/HN_3, and $NaClO_4$. The curves in Figure 1 clearly exhibit an induction period and autocatalytic behavior, and both the concentration and rate of Co(III) formation depend on the employed S(IV) concentration. In these experiments an excess of Co(II) is used and the concentration of the Co(III) produced is 1.3 times the sulfite concentration when [N_3^-] = 0.1 M. The later parts of the absorbance/time curves can be used to calculate pseudo-first-order rate constants by plotting ln (Δabs) versus time. The obtained first-order rate constants, k_{obs}, although subjected to large error limits due to the initial interference of the autocatalytic behavior, do depend linearly on the sulfite concentration, as demonstrated in Figure 2. The reaction also exhibits a remarkable dependence on the free azide concentration, as shown in Figure 3. The reaction is significantly faster at lower azide concentration, although the concentration of the Co(III) produced is also lower, which means that the catalyzed oxidation process is fast but less effective under such conditions (see further discussion). Similar induction periods and autocatalytic behavior have been reported for the Co(II)- and Fe(II)-catalyzed autoxidation of sulfur(IV) oxides.[17-19]

In order to investigate the autocatalytic nature of the process (Figures 1 and 3), experiments were performed in which Co(III) was initially added to the reaction mixture. For this purpose $Na_3Co(CO_3)_3$ was dissolved in azide buffer, and it rapidly aquates via decarboxylation to produce the cobalt(III) azide complex under the selected conditions. The initial Co(III) concentration was evaluated from the absorbance of the cobalt(III) azide complex at 365 nm. On the mixing of solutions containing Co(II), Co(III), N_3^-/HN_3, and $NaClO_4$ with sulfite in a stopped-flow instrument,

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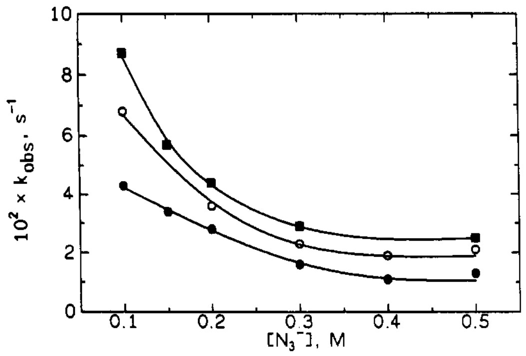

Figure 4. k_{obs} as a function of [N_3^-] for the oxidation of Co(II) at various S(IV) concentrations. Conditions: [Co(II)] = 5 × 10^{-4} M; $[Co(III)]_i$ = 3 × 10^{-5} M, [N_3^-]/[HN_3] = 5; pH = 5.0; [S(IV)] = 1 × 10^{-5} (●), 3 × 10^{-5} (○), 4 × 10^{-5} M (■); ionic strength = 1.0 M; temperature = 25 °C; [O_2] = 2 × 10^{-4} M.

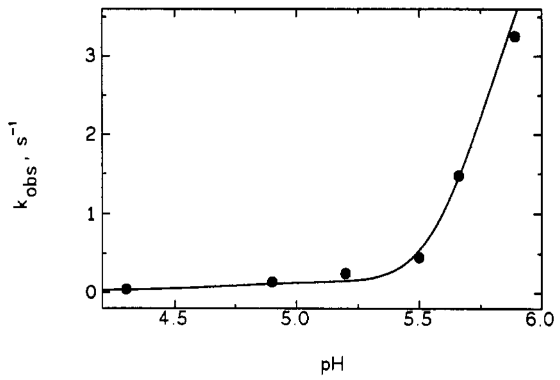

Figure 5. k_{obs} as a function of pH for the oxidation of Co(II) in azide medium. Conditions: [Co(II)] = 5 × 10^{-4} M; [N_3^-] = 0.1 M, $[Co(III)]_i$ = 3 × 10^{-5} M; [S(IV)] = 4 × 10^{-5} M; [O_2] = 2 × 10^{-4} M; ionic strength = 1.0 M; temperature = 25 °C.

the absorbance/time plots exhibited only a slight induction period similar to that reported before.[11] The first-order plots could be fitted after elapse of a few seconds, and reproducible rate constants were obtained. It should be mentioned that azide complexes of Co(III) are photosensitive and decompose to Co(II) and N_2,[20] which could under the influence of the intense light source of the stopped-flow instrument cause a slow subsequent absorbance decrease. However, this effect is negligible for reactions that are over in less than 100 s.

The influence of the added Co(III) concentration can clearly be seen from the plots of k_{obs} versus sulfite concentration as a function of the initial Co(III) concentration in Figure 2. These results can be described by the empirical rate law (2), where k_a

$$k_{obs} = k_a[Co(III)]_i + k_b[S(IV)] \qquad (2)$$

= 1013 ± 119 and k_b = 1444 ± 100 M^{-1} s^{-1} at 0.1 M N_3^- compared to k_a = 264 ± 31 and k_b = 400 ± 35 M^{-1} s^{-1} at 0.3 M N_3^- and 25 °C. The values of k_{obs} do depend on the azide concentration (Figure 4) and pH of the solution (Figure 5). For solutions at pH > 5.5 the initial Co(III) concentration was generated through the addition of sulfite (at 10^{-5} M level), since the dissolution of $Na_3[Co(CO_3)_3]$ is difficult under such conditions. The values of k_{obs} are not affected by the concentration of Co(II) and O_2, although both these species must be present for the reaction to occur. This means that we are dealing with a simultaneous oxidation process of both Co(II) and S(IV) by dissolved O_2 in which the participation of Co(II) and O_2 occur in non-rate-determining steps.

Reduction of Cobalt(III) Azide Complexes by Sulfite. In order to resolve the autocatalytic nature of the oxidation process and the role of Co(III) complexes, we first turn to a study of the redox

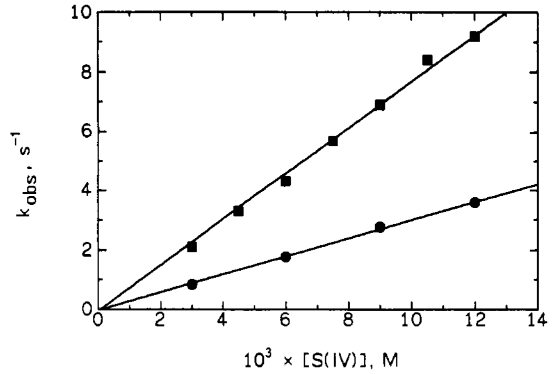

Figure 6. k_{obs} as a function of [S(IV)] for the reduction of Co(III) in azide medium. Conditions: [Co(III)] = 4 × 10^{-5} M; [N_3^-]/[HN_3] = 5; [N_3^-] = 0.1 (■), 0.3 M (●); pH = 5.0; [O_2] = 2 × 10^{-4} M; ionic strength = 1.0 M; temperature = 25 °C.

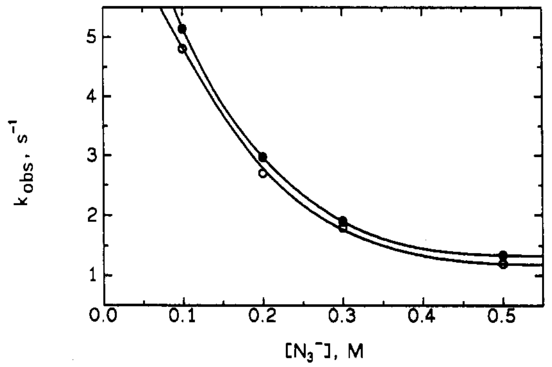

Figure 7. k_{obs} as a function of [N_3^-] for the reduction of Co(III) in azide medium. Conditions: [Co(III)] = 4 × 10^{-5} M; [N_3^-]/[HN_3] = 5; pH = 5.2; [S(IV)] = 6 × 10^{-3} M; ionic strength = 1.0 M; temperature = 25 °C; [O_2] = 0 (●), 2 × 10^{-4} M (○).

reactions of Co(III) with sulfite in azide medium and then return to the overall mechanism. In these experiments azide complexes of Co(III) were prepared in solution by dissolving $Na_3[Co(CO_3)_3]$ in acidic azide buffer, followed by deaeration with N_2 for 5 min to remove the released CO_2. The concentration of the Co(III) solution was determined from the known extinction coefficient of the azide complex. When sulfite is added to such a solution the absorbance maximum at 365 nm decreases rapidly due to the reduction of Co(III) to Co(II) via the intermediate formation of SO_3^-, for which the overall reaction is given in (3).[12] Addition

$$2Co(N_3)_4^- + SO_3^{2-} + H_2O \rightarrow 2N_3^- + 2HN_3 + 2Co(N_3)_2 + SO_4^{2-} \qquad (3)$$

of oxygen to the reduced solution rapidly reproduces the Co(III) complex again in the presence of excess sulfite. Similar experiments demonstrated that the isolated carbonate complex of Co(III) was contaminated with some traces of Co(II), which caused a slight initial increase in the Co(III) concentration when the complex is treated with sulfite in the presence of O_2. The cobalt(III) azide complex prepared from the carbonato complex also exhibits a slow spontaneous redox reaction especially at lower pH, for instance at [N_3^-]:[HN_3] ratio of 1:1. In all experiments it could clearly be seen that the cobalt(III) azide complex is rapidly reduced by sulfite in the absence of O_2, and the produced Co(II) complex can be reoxidized to Co(III) on addition of O_2 and sulfite.

The redox reaction was followed under anaerobic and pseudo-first-order conditions, i.e. an excess of sulfite, and the observed kinetic traces exhibited excellent first-order behavior. The reaction of Co(III) with sulfite is accompanied by an absorbance decrease at 400 nm due to the reduction of Co(III), and the observed rate constant, k_{obs}, depends linearly on the sulfite concentration, as shown in Figure 6. The data can be described by the relationship in (4) for which k_c = 811 ± 20 and 309 ± 9 M^{-1} s^{-1} at 0.1 and

$$k_{obs} = k_c[S(IV)] \qquad (4)$$

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0.3 M N_3^-, respectively. The decrease in k_c with increasing $[N_3^-]$ is further demonstrated by the data in Figure 7, from which it is also seen that this redox reaction is not affected by the presence of oxygen under the selected experimental conditions, viz. an excess of sulfite. Furthermore, k_{obs} was found to be independent of pH in the range $4.4 \leq pH \leq 5.7$. Very remarkable is the observation that the kinetic data reported in Figures 6 and 7 are qualitatively in a close agreement with those reported for the oxidation of Co(II) in Figures 2 and 4, respectively. As our further discussion will indicate, this agreement is also valid for a quantitative comparison of the data. It demonstrates that the same mechanism and rate-determining step must be operative during the reduction of Co(III) by sulfite and the oxidation of Co(II) by O_2 in the presence of sulfite in an azide medium.

Overall Mechanism. The above observations lead to the suggestion that the oxidation of Co(II) in azide medium in the presence of O_2 and sulfite is catalyzed by Co(III) at a rate that corresponds approximately to the reduction of Co(III) by sulfite in azide medium. The autocatalytic behavior observed for the oxidation process can in general terms be described by the reaction sequence in (5),[21,22] where A represents sulfur(IV) oxide and P

$$\mathrm{A} + \mathrm{P} \xrightarrow{k} \mathrm{B}$$

$$\mathrm{B} \rightarrow \xrightarrow{\text{fast}} \rightarrow (a + 1)\mathrm{P}$$

$$\text{net:} \qquad \mathrm{A} \rightarrow a\mathrm{P} \qquad (5)$$

the cobalt(III) azide complex (i.e. oxidation product) in the present study. In this reaction sequence the formation of the intermediate B (SO_3^- in the present study) is rate-determining and is followed by a series of subsequent fast steps during which $(a + 1)$P is produced to account for the overall reaction ratio of A:P = 1:a. If $[A] = A_0 - x$ and $[P] = P_0 + ax$, where the subscript zero indicates the initial concentration, the rate law for such a process is given by the expression in (6). Integration of this expression

$$dx/dt = k(A_0 - x)(P_0 + ax) \qquad (6)$$

results in (7),[22] which can be rewritten in the form of (8). Under

$$\frac{1}{P_0 + aA_0} \ln \left[\frac{A_0(P_0 + ax)}{P_0(A_0 - x)} \right] = kt \qquad (7)$$

$$\ln (P_0/A_0) - \ln (P_0 + ax) + \ln (A_0 - x) = -k(P_0 + aA_0)t \qquad (8)$$

the conditions of the kinetic measurements, P was introduced from the start to minimize the autocatalytic part of the process and the kinetic traces were only fitted from the point of maximum rate, i.e. maximum $\Delta abs/\Delta t$ in Figures 1 and 3 (see earlier discussion). From (6) it can be shown that the maximum rate is reached at $(P_0 + ax)/(A_0 - x) = a$. From this point on $(P_0 + ax)$ will increase to $(P_0 + aA_0)$, whereas $(A_0 - x)$ will decrease to zero. Since $\ln (P_0/A_0)$ will be constant during the reaction, it follows that the later part of the kinetic trace is dictated by $\ln (A_0 - x)$ (as evidenced by the formation of the cobalt(III) azide complex), which exhibits first-order behavior with the observed rate constant given in (9). Under these conditions (8) describes a typical pseudo-first-order process.

$$k_{obs} = k(P_0 + aA_0) \qquad (9)$$

A comparison with the reported kinetic data underlines the validity of the suggested mechanism. (9) is of the same form as (2) with $k = k_a$ and $ak = k_b$, from which it follows that $k = 1013$ $M^{-1}\,s^{-1}$ and $a = 1.44$ for $[N_3^-] = 0.1$ M and $k = 265$ $M^{-1}\,s^{-1}$ and $a = 1.5$ for $[N_3^-] = 0.3$ M. In fact the ratio between the S(IV) oxidized and the Co(III) produced (i.e. a) was found spectrophotometrically to be 1.3 and 1.5 at $[N_3^-] = 0.1$ and 0.3 M, respectively. These values are very close to the kinetically determined values reported above and indicate that the factor "a" does not depend strongly on the azide concentration, i.e. the nature of the cobalt azide complex. It follows that the kinetic data in Figure 2 can be fitted with (10), as shown in Figure 8, with $k = 1033 \pm 57$ and 281 ± 23 $M^{-1}\,s^{-1}$ at $[N_3^-] = 0.1$ and 0.3 M, respectively, and $a = 1.5$ in comparison to (9).

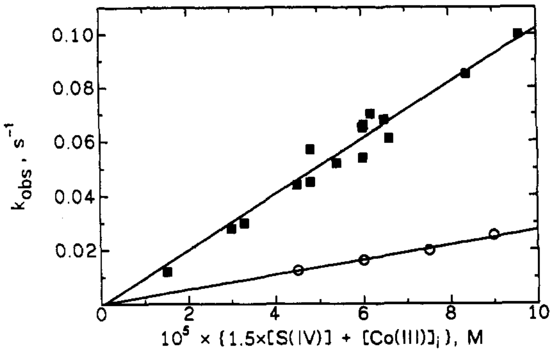

Figure 8. Plot of k_{obs} versus $\{1.5[S(IV)] + [Co(III)]_i\}$ for the oxidation of Co(II) in azide medium. Conditions: (■) data from Figure 2; (○) $[Co(II)] = 5 \times 10^{-4}$ M, $[N_3^-] = 0.3$ M, $[HN_3] = 0.06$ M, $[Co(III)]_i = 3 \times 10^{-5}$ M, pH = 5.1, $[O_2] = 2 \times 10^{-4}$ M.

$$k_{obs} = k\{[Co(III)]_i + 1.5[S(IV)]\} \qquad (10)$$

The overall suggested mechanism for the sulfite-induced autoxidation process is given in Scheme I, which is to a large extent based on reactions suggested in the literature.[23-27] Rate and acid dissociation constants are included in Scheme I where available. It is suggested that a cobalt(III) azide complex is responsible for the initiation of the process by reacting with sulfite to produce the sulfite radical SO_3^-. The first two reactions in the scheme are included to account for the long induction periods and low catalytic activity observed in the absence of initially added Co(III). The sulfite radical rapidly reacts with O_2 to produce SO_5^-, which is a strong oxidant and oxidizes Co(II) to Co(III). The produced peroxymonosulfate (HSO_5^- at the pH of this investigation) can subsequently react[6,26,27] with more Co(II) to produce Co(III), SO_4^{2-}, and OH radicals or OH^-. According to the set of reactions more Co(III) is produced than used in the rate determining step in order to account for the autocatalytic behavior. In addition, a number of possible chain propagation reactions are included in which more SO_3^- can be produced, which reacts almost in a diffusion-controlled manner with O_2, i.e. significantly faster than its recombination process, to produce $S_2O_6^{2-}$.[24]

It is important to note that the oxidation of Co(II) by HSO_5^- is expected to be considerably slower than the oxidation by SO_5^-, on the basis of the behavior of these species with SO_3^{2-} (see the quoted rate constants in Scheme I). The reaction of the OH radical with HSO_3^-/SO_3^{2-} is significantly faster than with HSO_5^-, such that the latter reaction may not be very important. A series of possible product formation and termination reactions are included in Scheme I, of which the exact details are still not fully understood.[23,25] The main oxidation product of S(IV) is SO_4^{2-} under the selected conditions, and no information on the possible formation of $S_2O_6^{2-}$ and $S_2O_8^{2-}$ as suggested in the scheme is presently available. Important is the fact that the formation of the SO_3^- radical is the rate-determining step, and all subsequent reactions are fast and do not affect the observed kinetics but do affect the observed stoichiometry. This then accounts for our observation that the oxidation rate constant is independent of the Co(II) and O_2 concentrations, as long as these species are present in solution. Furthermore, the experimentally determined value of k should be in agreement with that measured directly in the

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Scheme I. Suggested Mechanism[a]

Initiation (in the absence of added M(III)):

$$\mathrm{M(II)} + \mathrm{O_2} \longrightarrow \mathrm{M(III)} + \mathrm{O_2^-}$$

or $$\mathrm{M(II)(SO_3)_x} + \mathrm{O_2} \longrightarrow \mathrm{M(III)(SO_3)_x} + \mathrm{O_2^-}$$

Autocatalysis:

$$\mathrm{M(III)} + \mathrm{SO_3^{2-}} \xrightarrow{k} \mathrm{M(II)} + \mathrm{SO_3^-} \qquad \text{slow}$$

$$\mathrm{SO_3^-} + \mathrm{O_2} \longrightarrow \mathrm{SO_5^-} \qquad 1.5\times10^{9}\ \mathrm{M^{-1}\,s^{-1}}$$

$$\mathrm{M(II)} + \mathrm{SO_5^-} \longrightarrow \mathrm{M(III)} + \mathrm{SO_5^{2-}}$$

$$\mathrm{SO_5^{2-}} + \mathrm{H^+} \rightleftharpoons \mathrm{HSO_5^-} \qquad \mathrm{p}K_a = 9.4$$

$$\mathrm{M(II)} + \mathrm{HSO_5^-} \longrightarrow \mathrm{M(III)} + \mathrm{SO_4^{2-}} + \mathrm{OH}$$

or $$\mathrm{M(II)} + \mathrm{HSO_5^-} \longrightarrow \mathrm{M(III)} + \mathrm{SO_4^-} + \mathrm{OH^-}$$

$$\mathrm{M(II)} + \mathrm{SO_4^-} \longrightarrow \mathrm{M(III)} + \mathrm{SO_4^{2-}}$$

Chain propagation:

$$\mathrm{HSO_3^-/SO_3^{2-}} + \mathrm{OH} \longrightarrow \mathrm{SO_3^-} + \mathrm{H_2O/OH^-} \qquad 4\times10^{9}\ \mathrm{M^{-1}\,s^{-1}}$$

$$\mathrm{HSO_5^-} + \mathrm{OH} \longrightarrow \mathrm{SO_5^-} + \mathrm{H_2O} \qquad 1.7\times10^{7}\ \mathrm{M^{-1}\,s^{-1}}$$

$$\mathrm{SO_5^-} + \mathrm{SO_3^{2-}} \longrightarrow \mathrm{SO_5^{2-}} + \mathrm{SO_3^-} \qquad 1.3\times10^{7}\ \mathrm{M^{-1}\,s^{-1}}$$

$$\text{and} \longrightarrow \mathrm{SO_4^{2-}} + \mathrm{SO_4^-}$$

$$\mathrm{SO_5^-} + \mathrm{HSO_3^-} \longrightarrow \mathrm{HSO_5^-} + \mathrm{SO_3^-} \qquad <3\times10^{5}\ \mathrm{M^{-1}\,s^{-1}}$$

$$\mathrm{SO_5^-} + \mathrm{SO_5^-} \longrightarrow 2\mathrm{SO_4^-} + \mathrm{O_2} \qquad 6\times10^{8}\ \mathrm{M^{-1}\,s^{-1}}$$

$$\mathrm{SO_4^-} + \mathrm{SO_3^{2-}} \longrightarrow \mathrm{SO_4^{2-}} + \mathrm{SO_3^-} \qquad 5\times10^{8}\ \mathrm{M^{-1}\,s^{-1}}$$

$$\mathrm{SO_4^-} + \mathrm{HSO_3^-} \longrightarrow \mathrm{SO_4^{2-}} + \mathrm{SO_3^-} + \mathrm{H^+} \qquad 1.1\times10^{9}\ \mathrm{M^{-1}\,s^{-1}}$$

Product formation/termination:

$$\mathrm{HSO_5^-} + \mathrm{SO_3^{2-}} \longrightarrow 2\mathrm{SO_4^{2-}} + \mathrm{H^+} \qquad 3.5\times10^{2}\ \mathrm{M^{-1}\,s^{-1}}$$

$$\mathrm{HSO_5^-} + \mathrm{HSO_3^-} \longrightarrow 2\mathrm{SO_4^{2-}} + 2\mathrm{H^+} \qquad 2.6\times10^{6}\ \mathrm{M^{-1}\,s^{-1}}$$

$$\mathrm{SO_3^-} + \mathrm{SO_3^-} \longrightarrow \mathrm{S_2O_6^{2-}} \qquad 2.5\times10^{8}\ \mathrm{M^{-1}\,s^{-1}}$$

$$\mathrm{SO_4^-} + \mathrm{SO_4^-} \longrightarrow \mathrm{S_2O_8^{2-}} \qquad 4.4\times10^{8}\ \mathrm{M^{-1}\,s^{-1}}$$

$$\mathrm{SO_5^-} + \mathrm{SO_5^-} \longrightarrow \mathrm{S_2O_8^{2-}} + \mathrm{O_2} \qquad 1.4\times10^{8}\ \mathrm{M^{-1}\,s^{-1}}$$

$$\mathrm{SO_5^-} + \mathrm{SO_3^-} \longrightarrow \mathrm{S_2O_6^{2-}} + \mathrm{O_2}$$

$$\mathrm{SO_5^-} + \mathrm{O_2^-} \longrightarrow \mathrm{SO_5^{2-}} + \mathrm{O_2}$$

$$\mathrm{O_2^-} + \mathrm{H^+} \rightleftharpoons \mathrm{HO_2} \qquad \mathrm{p}K_a = 4.8$$

$$\mathrm{O_2^-} + \mathrm{HO_2} \longrightarrow \mathrm{HO_2^-} + \mathrm{O_2} \qquad 9.7\times10^{8}\ \mathrm{M^{-1}\,s^{-1}}$$

$$\mathrm{HO_2^-} + \mathrm{H^+} \rightleftharpoons \mathrm{H_2O_2} \qquad \mathrm{p}K_a = 11.6$$

$$\mathrm{HSO_3^-/SO_3^{2-}} + \mathrm{H_2O_2} \longrightarrow \mathrm{HSO_4^-/SO_4^{2-}} + \mathrm{H_2O}$$

[a] M = Co–N_3 complex.

reaction of Co(III) with sulfite in azide medium. This agreement has been referred to above (compare Figures 6 and 7 with Figures 2 and 4, respectively), and even the numerical agreement is fairly good, considering the assumptions and simplifications made in the treatment of the autocatalytic process.

The suggested mechanism in Scheme I can account for the observed kinetic traces and concentration dependencies. The effectiveness of the autocatalytic process is controlled by the competition of Co(II) and SO_3^{2-} for HSO_5^-, as indicated in the scheme. The effect of pH and $[N_3^-]$ on the observed rate constant (Figures 4, 5, and 7) must be due to the nature of the azide complexes and S(IV) species that participate in the rate-determining step. The pH dependence can be related to either the participation of cobalt(III) hydroxo species or a shift in the HSO_3^-/SO_3^{2-} equilibrium (pK_a = 6.3[2]) that will lead to an increase in the redox rate constant at pH > 5.5. Although cobalt(III) hydroxo complexes are usually very inert, deprotonation of a coordinated water molecule may lead to a trans labilization of coordinated azide, which in turn may enable an inner-sphere redox reaction with sulfite. The $[N_3^-]$ dependencies reported in Figures 4 and 7 must be related to the speciation of the cobalt(III) azide complexes.[16] The data indicate that a limiting rate constant is reached at 0.5 M N_3^-, indicating that the $Co^{III}(N_3)_5$ or $Co^{III}(N_3)_6$ complexes are less redox sensitive than the less substituted complexes. This in turn accounts for the observation (Figure 3) that more Co(III) is produced under such conditions, since the reverse decomposition rate is slower. This is also in agreement with the fact that the reduction potential of the cobalt(III) azide complexes decreases with increasing azide concentration.[28] A similar result was reported for a series of chloro and bromo complexes of Ir(IV),[29] i.e. a decrease in reduction potential with increasing number of chloride and bromide ligands, and can be understood in terms of the relative electron density on the metal center; the lower the

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electron density, the higher the reduction potential and the faster the reaction. According to the available stability constants[16] the main species present in solution will be $Co^{III}(N_3)_4$ and $Co^{III}(N_3)_6$ for the investigated $[N_3^-]$ range. For instance, the general mechanism outlined in (11) can account in a qualitative way for the observed $[N_3^-]$ dependence, in which k_1 and k_2 involve substitution (anation) followed by inner-sphere electron transfer.

$$Co^{III}(N_3)_4(H_2O)_2^- + N_3^- \overset{K}{\rightleftharpoons} Co^{III}(N_3)_5H_2O^{2-} + H_2O$$

$$Co^{III}(N_3)_4(H_2O)_2^- + HSO_3^-/SO_3^{2-} \xrightarrow{k_1} Co(II) + 4N_3^- + SO_3^- \quad (11)$$

$$Co^{III}(N_3)_5H_2O^{2-} + HSO_3^-/SO_3^{2-} \xrightarrow{k_2} Co(II) + 5N_3 + SO_3^-$$

The rate law for this mechanism under the condition that $1 + K[N_3^-] \approx K[N_3^-]$ is given in (12), from which it follows that k_{obs}

$$k_{obs} = \left(\frac{k_1}{K[N_3^-]} + k_2\right)[S(IV)] \qquad (12)$$

should depend linearly on $[N_3^-]^{-1}$. This is indeed the case for the data in Figure 7, and the intercept of such a plot (k_2) is in good agreement with the limiting rate constant reached at high $[N_3^-]$. Such relationships could further indicate that the less substituted cobalt(III) azide complexes may undergo an inner-sphere redox reaction with sulfite involving the substitution of a coordinated water molecule, whereas the more substituted species may follow an outer-sphere mechanism. However, the limited available data and complexity of the system do not allow a definite assignment of the species involved.

In conclusion, we would like to point at the rather surprising finding of this study that the rate-determining step for sulfite-catalyzed autoxidation of the cobalt(II) azide complexes is the reduction of the cobalt(III) azide complexes by sulfite to produce the sulfite radical SO_3^-. This mechanistic aspect may play an important role in metal-catalyzed autoxidation reactions of sulfur(IV) oxides and account for the catalytic role of species such as Fe(II/III) and Mn(II/III).[7,19]

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Solid-State ^{31}P NMR and X-ray Crystallographic Studies of Tertiary Phosphines and Their Derivatives

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High-resolution, solid-state ^{31}P NMR spectra of PPh_3 and its oxide, sulfide, and selenide and PCy_3 and its oxide, sulfide, and selenide are presented and interpreted in terms of reported space group information from X-ray crystallographic studies. The spectra of $Ph_2PCH_2CH_2PPh_2$ and $Ph_2PCH_2PPh_2$ are similarly described. In order to fully interpret the NMR spectra, the X-ray crystal structures of PCy_3 (**1**), $OPCy_3$ (**2**), and $SePCy_3$ (**3**) were determined. Data are as follows: **1**, fw = 280.44, trigonal, $P3_1$, a = 9.893 (2) Å, c = 15.446 (3) Å, V = 1309.2 Å^3, Z = 3, D_x = 1.07 g cm^{-3}, λ(Mo Kα_1) = 0.709 30 Å, μ = 1.4 cm^{-1}, $F(000)$ = 468, T = 294 (1) K, R = 0.045 for 1092 unique reflections with $F^2 > 3\sigma(F^2)$; **2**, fw = 296.44, triclinic, $P\bar{1}$, a = 9.799 (4) Å, b = 16.402 (6) Å, c = 17.067 (6) Å, α = 101.30 (3)°, β = 90.39 (3)°, γ = 99.86 (3)°, V = 2647.8 Å^3, Z = 6, D_x = 1.23 g cm^{-3}, λ(Mo K$\bar{\alpha}$) = 0.710 73 Å, μ = 1.6 cm^{-1}, $F(000)$ = 1086, T = 294 (1) K, R = 0.051 for 4939 unique reflections with $F^2 > 3\sigma(F^2)$; **3**, fw = 359.40, orthorhombic, $Pnma$, a = 11.110 (1) Å, b = 15.803 (2) Å, c = 10.364 (1) Å, V = 1819.6 Å^3, Z = 4, D_x = 1.31 g cm^{-3}, λ(Mo K$\bar{\alpha}$) = 0.710 73 Å, μ = 21.2 cm^{-1}, $F(000)$ = 760, T = 294 (1) K, R = 0.034 for 1308 unique reflections with $F^2 > 3\sigma(F^2)$.

Introduction

CP/MAS NMR methods[1] provide structural data on solid-phase materials that may serve as an important bridge between high-resolution solution NMR data and information generated by single-crystal X-ray diffraction. In this context, it is important that the differences in these analytical methods, particularly with respect to differentiation of subtle structural changes, be understood.

Data collected by high-resolution solution NMR methods and by CP/MAS solid-state NMR techniques have been compared and contrasted by many workers, and Fyfe[2] has summarized many of the important results. Considering CP/MAS ^{31}P NMR and high-resolution solution ^{31}P or $^{31}P\{^1H\}$ NMR methods as repre-

Table I. Solution and Solid-State ^{31}P NMR Data

compd	soln data:[a] δ(P)/ppm	solid-state data: δ(P)/ppm	compd	soln data:[a] δ(P)/ppm	solid-state data: δ(P)/ppm
PPh_3	−5.31	−7.20	$SPCy_3$	61.92	63.12
$OPPh_3$	29.61	28.99	$SePCy_3$	58.35[d]	60.61[e]
$SPPh_3$	43.36	46.37	dppm	−22.48	−22.33[f]
$SePPh_3$	35.36[b]	37.91[c]			−23.54[f]
PCy_3	11.13	9.28	dppe	−12.59	−9.95
$OPCy_3$	49.84	49.37			
		50.18			

[a] All solution $^{31}P\{^1H\}$ NMR data were measured in $CDCl_3$ at room temperature and referenced to external 85% H_3PO_4. [b] $^1J(^{31}P,^{77}Se)$ = 728 Hz. [c] $^1J(^{31}P,^{77}Se)$ = 737 Hz. [d] $^1J(^{31}P,^{77}Se)$ = 673 Hz. [e] $^1J(^{31}P,^{77}Se)$ = 684 Hz. [f] $^2J(^{31}P,^{31}P)$ = 210 Hz.

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