Kinetics and Mechanism for the Redox Reaction between Hexaaquathallium(III) and Sulfur Dioxide in Acidic Aqueous Solution

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Oxidation of dissolved sulfur dioxide, $SO_2{\cdot}nH_2O$, HSO_3^- and SO_3^{2-}, by hexaaquathallium(III) has been studied in acidic aqueous solution with ionic strength 1.0 mol dm^{-3} at 25 °C. The stoichiometry of the reaction has been determined: $[Tl(H_2O)_6]^{3+} + SO_2(aq) + 2H_2O \longrightarrow [Tl(H_2O)_6]^+ + HSO_4^- + 3H^+$. The kinetics has been studied by use of stopped-flow spectrophotometry under pseudo-first-order conditions with either S^{IV} or Tl^{III} in excess. The reaction is first order in both $[S^{IV}]$ and $[Tl^{III}]$ and has a complex $[H^+]$ dependence. The rate decreases with increasing $[H^+]$ in the range $0.1 < [H^+] < 1.0$ mol dm^{-3}. The results are interpreted in terms of a reaction mechanism where sulfito complexes are formed by reaction between $[Tl(H_2O)_6]^{3+}$ or $[Tl(H_2O)_5(OH)]^{2+}$ and HSO_3^-. These complexes decompose to the products $[Tl(H_2O)_6]^+$ and HSO_4^- by intramolecular inner-sphere electron-transfer processes. The thallium(III) sulfito complexes are weak, as indicated by the absence of any transient absorbance peaks in the UV region. Potentiometric measurements of the oxygen concentration and spectrophotometric measurements showed that Tl^{III} does not initiate a free-radical chain oxidation of S^{IV} by dissolved oxygen.

In aqueous solution, sulfur(IV) in the form of sulfur dioxide is present as an equilibrium mixture of $SO_2{\cdot}nH_2O$, HSO_3^- and SO_3^{2-}. Oxidation of this mixture to dithionate and/or sulfate by various metal complexes has been the subject of a number of studies,[1–31] mainly by use of one-electron oxidants such as Co^{III},[1,3–9,11,12] Rh^{III},[2] Cr^{III},[2,10] Fe^{III},[13–18] Mo^{V},[19] W^{V},[19] Mn^{III},[20,21] Ru^{III},[22] Ir^{IV},[23] Os^{III}[23] and Cu^{III}.[30] Only a few studies of complementary redox reactions with two-electron oxidants, *viz.* complexes of Au^{III}, Ag^{III} and Pt^{IV}, have been reported so far.[14–29] In order further to elucidate the kinetics and mechanism for those complementary redox processes, we have studied the oxidation of S^{IV} by use of some complexes of Pt^{IV} (ref. 28) and Au^{III}.[30] In the present paper we report on the oxidation of S^{IV} by $[Tl(H_2O)_6]^{3+}$ and $[Tl(H_2O)_5(OH)]^{2+}$ in acidic aqueous solution. Thallium(III) has been used as a reagent for quantitation of sulfite,[32] but the mechanism for the redox reaction has not been elucidated.

In some cases, redox reactions between metal complexes and sulfur(IV) are very sensitive to the presence of dissolved molecular oxygen.[23,31] Metal ions may initiate a free-radical chain reaction similar to that occurring in the photoinduced autoxidation of S^{IV}.[33] Some metal complexes, for example Fe^{III} (ref. 34) and Mn^{III},[35] not only initiate the chain reaction but take part in a catalytic cycle. As far as we know, there have been no reports on two-electron oxidants initiating or catalysing the autoxidation of S^{IV}. This aspect of the thallium(III) reaction has also been elucidated in the present study.

Experimental

Chemicals and Solutions.—Thallium(I) nitrate (Merck pa) was used for recording a reference spectrum of Tl^{I}. A stock solution of hexaaquathallium(III) (0.184 mol dm^{-3}) was prepared by dissolving Tl_2O_3 (Janssen Chimica, 99%) (*ca.* 10 g) in concentrated perchloric acid (Merck pa) (100 cm^3) at *ca.* 50 °C. Water (130 cm^3) was added and the solution was filtered through a Millipore filter in order to remove traces of undissolved Tl_2O_3. The thallium concentration was determined iodometrically.[36] The solution was stable during 2 months.

Stock solutions of sulfur(IV) (*ca.* 50 mmol dm^{-3}) were prepared fresh before each set of experiments by dissolving Na_2SO_3 (Merck pa) (*ca.* 0.65 g) in an air-saturated ionic medium (100 cm^3). In these solutions $0.1 < [H^+] < 1.0$ mol dm^{-3} and the ionic strength was adjusted to 1.0 mol dm^{-3} by use of sodium perchlorate (Merck pa) and perchloric acid (Merck pa). The concentration of sulfur(IV) was determined iodometrically[37] and shown to be constant during the course of the experiments.

Solutions of Tl^{III} and S^{IV} were prepared by dilution of the stock solutions with ionic medium, $0.1 < [HClO_4] < 1.0$ and $0.1 < [NaClO_4] < 1.0$ mol dm^{-3}. The hydrogen-ion concentrations were determined by titration with standard solutions of sodium hydroxide (Merck pa). The ionic strength was 1.0 mol dm^{-3} in all experiments. Water was doubly distilled from quartz. During 2 h there was no significant decrease in absorbance at the 278 nm maximum of $SO_2{\cdot}nH_2O$ for a solution of 1.5 mmol dm^{-3} S^{IV} in 1.0 mol dm^{-3} $HClO_4$. Thus, the diluted sulfur(IV) solutions were also stable during the time they were used for the experiments.

Spectral and Kinetic Measurements.—Spectra were recorded by use of a Milton-Roy 3000 diode-array spectrophotometer and thermostatted 1 cm quartz Suprasil cells. The kinetics was followed by use of a modified Durrum-Gibson stopped-flow instrument. All experiments were performed at 25.0 ± 0.1 °C. The kinetics was evaluated with an on-line OLIS least-squares minimizing program,[38] implemented on a Victor V286A personal computer.

Check of Autoxidation.—The concentration of dissolved oxygen in a freshly prepared solution of 1.2 mmol dm^{-3} S^{IV} in 0.1 mol dm^{-3} $HClO_4$ and 0.9 mol dm^{-3} $NaClO_4$ was measured during 75 min by use of an Orion Research oxygen electrode, model 97-08, connected to an EA 920 expandable ion analyser. The experiment was repeated with identical sulfur(IV) solutions in the presence of either 3×10^{-5} mol dm^{-3} Tl^{III} or Fe^{III} [as $Fe(NO_3)_3{\cdot}9H_2O$, Merck pa]. The concentration of dissolved oxygen in air-saturated water is *ca.* 2.5×10^{-4} mol dm^{-3}, so if autoxidation of S^{IV} occurs in these experiments the dissolved oxygen should be depleted. In the absence of Tl^{III} and Fe^{III}, the oxygen concentration decreased by less than 2.5% during 75 min, presumably due to autoxidation of S^{IV} catalysed by trace impurities of metal ions (*cf.* ref. 35). In the presence of 3×10^{-5} mol dm^{-3} Tl^{III} no significant difference in the decrease of dissolved oxygen was detected. The concentration of oxygen decreased by only *ca.* 5% after 210 min. In the presence of 3×10^{-5} mol dm^{-3} Fe^{III}, on the other hand, the dissolved oxygen was depleted after *ca.* 180 min, showing the catalytic effect of Fe^{III}.[34]

Equal volumes of 3.0 mmol dm^{-3} S^{IV} and 2.0 mmol dm^{-3} Tl^{III} in 1.0 mol dm^{-3} $HClO_4$ were mixed directly in a spectrophotometric cell and the absorbance of $SO_2{\cdot}nH_2O$ at 278 nm was monitored by use of the diode-array spectrophotometer. The absorbance instantly dropped from 0.54 to 0.24 and then remained constant for 2 h; 1.0 mmol dm^{-3} Tl^{III} in 1.0 mol dm^{-3} $HClO_4$ has an absorbance of 0.06 which means that 0.5 mmol dm^{-3} S^{IV} remains in solution after the reduction of 1.0 mmol dm^{-3} Tl^{III}. Both this experiment and the potentiometric measurements of the oxygen concentration show that Tl^{III} neither initiates nor catalyses the autoxidation of S^{IV}.

Results

Stoichiometry.—The spectrum of an equilibrium solution prepared by mixing equal volumes of 1.0×10^{-4} mol dm^{-3} Tl^{III} and 1.0×10^{-4} mol dm^{-3} S^{IV} in 0.1 mol dm^{-3} $HClO_4$ and 0.9 mol dm^{-3} $NaClO_4$ is identical to a reference spectrum of $[Tl(H_2O)_6]^+$ recorded separately in the same ionic medium. Thus, the final product of reduction of Tl^{III} with S^{IV} is Tl^{I}.

The stoichiometry of the redox reaction was determined by spectrophotometric measurements. Eleven solutions with 4.8 mmol dm^{-3} S^{IV} and $[Tl^{III}] \leqslant 6.0$ mmol dm^{-3} were prepared in 1.0 mol dm^{-3} ionic medium. The solutions were aged for *ca.* 15 min and their absorbances at 278 nm measured. Since neither Tl^{I} nor any possible product of the oxidation of S^{IV}, sulfate and dithionate, absorbs at this wavelength, the stoichiometry of the reaction can easily be determined from a plot of the absorbance *vs.* the concentration of Tl^{III}, Fig. 1. The stoichiometric factor is given by the intersection with the *x* axis. The experiment was repeated twice using $[HClO_4] = 0.5$ and 1.0 mol dm^{-3}, respectively. The mean value of the stoichiometric factor is 1.03. Thus, the stoichiometry is 1 : 1 for the reduction of Tl^{III} by S^{IV} in an acidic medium according to reaction (1).

$$[Tl(H_2O)_6]^{3+} + SO_2(aq) + 2H_2O \longrightarrow [Tl(H_2O)_6]^{+} + HSO_4^{-} + 3H^{+} \quad (1)$$

Kinetics.—In preliminary experiments the kinetics was followed at wavelengths between 210 and 350 nm by use of the stopped-flow instrument with different time bases. Only one reaction could be observed after mixing equal volumes of solutions of Tl^{III} and S^{IV}. Under some experimental conditions, it was possible to monitor this reaction by use of the absorbance increase at 213 nm where $[Tl(H_2O)_6]^+$ has a maximum. However, the high absorbance of Tl^{III}, HSO_3^- and SO_4^{2-} at wavelengths < 230 nm limited the possibilities to study the formation of Tl^{I} at shorter wavelengths. The compound $SO_2{\cdot}nH_2O$ has an absorbance maximum at 278 nm. At the concentration used the absorbance of Tl^{I} and Tl^{III} can be neglected at wavelengths > 250 nm, and HSO_3^- and SO_4^{2-} do not absorb at 278 nm either. Therefore, most experiments were performed at this wavelength, where the kinetics can be monitored as a decrease in absorbance.

Pseudo-first-order conditions were employed with either Tl^{III} or S^{IV} in at least ten-fold excess. With excess of Tl^{III}, the oxidation of S^{IV} was studied as a function of $[Tl^{III}]$ and $[H^+]$ using $2 \times 10^{-5} < [S^{IV}] < 1 \times 10^{-4}$ mol dm^{-3}, $0.2 < [Tl^{III}] < 7.0$ mmol dm^{-3} and $0.10 < [H^+] < 1.0$ mol dm^{-3}, Fig. 2. In all cases, perfect first-order fits were obtained by use of the non-linear least-squares minimizing program. Also, the

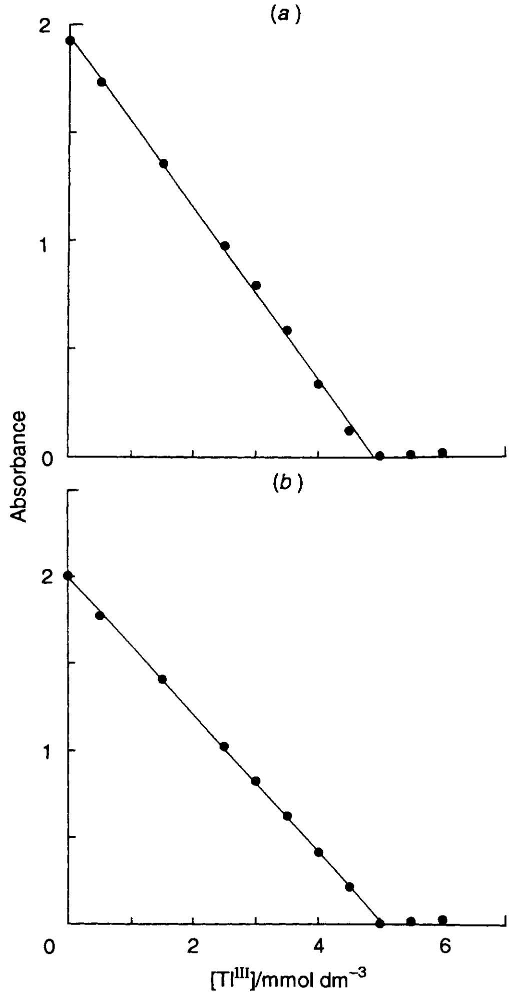


Fig. 1 Absorbance at 278 nm for solutions with constant $[S^{IV}]$ and increasing $[Tl^{III}]$: (*a*) $[S^{IV}] = 4.79$ mmol dm^{-3}, $[H^+] = 1.0$ mol dm^{-3}, $I = 1.0$ mol dm^{-3}; (*b*) $[S^{IV}] = 4.85$ mmol dm^{-3}, $[H^+] = 0.5$ mol dm^{-3}, $I = 1.0$ mol dm^{-3}. The lines represent the best fits obtained by use of linear regression analysis

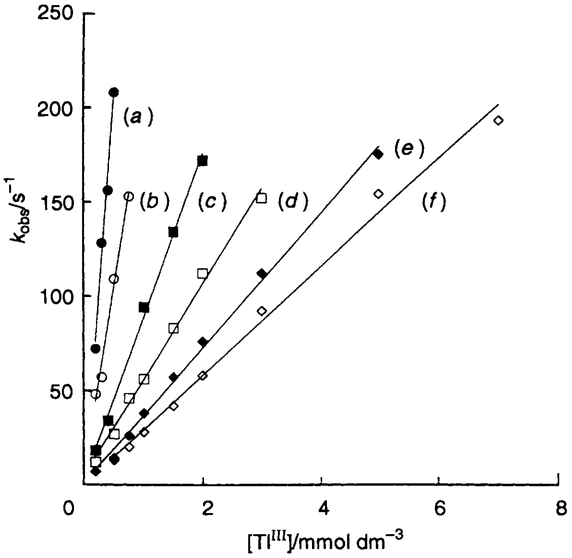


Fig. 2 Observed rate constant k_{obs} as a function of $[Tl^{III}]$ and $[H^+]$. Conditions: $2 \times 10^{-5} < [S^{IV}] < 1 \times 10^{-4}$ mol dm^{-3}, $I = 1.0$ mol dm^{-3}, 25 °C, $[H^+] = 0.1$ (*a*), 0.2 (*b*), 0.4 (*c*), 0.6 (*d*), 0.8 (*e*), or 1.0 mol dm^{-3} (*f*). The lines represent the best fits to the experimental data obtained by use of linear regression analysis

rate constants were independent of the sulfur(IV) concentration in the presence of an excess of Tl^{III}, emphasizing the first-order dependence with respect to $[S^{IV}]$.

The investigation of the $[H^+]$ dependence of the reaction was limited by the increase of the rate of reaction and by precipitation of thallium(III) hydroxide with decreasing $[H^+]$. Under the present experimental conditions, using thallium(III) in excess, the reaction was too fast to be monitored by use of the stopped-flow technique for pH > 1. Decreasing the total concentraton of S^{IV} and Tl^{III} in order to slow down the reaction and suppress the hydroxide precipitation at higher pH was not feasible since the change in absorbance at 278 nm then became too small. At pH 1 the lower limit of the sulfur(IV) concentration for accurate evaluation of the kinetics was approximately 2×10^{-5} mol dm^{-3}.

Experiments with S^{IV} in excess were performed under the following conditions: $0.25 < [S^{IV}] < 2.5$ mmol dm^{-3}, $2.5 \times 10^{-5} < [Tl^{III}] < 2.5 \times 10^{-4}$ mol dm^{-3} and $0.6 < [H^+] < 1.0$ mol dm^{-3}. They are summarized in Fig. 3. The kinetic traces using S^{IV} in excess were much noisier than those obtained using Tl^{III} in excess due to the strong background absorbance of $SO_2 \cdot nH_2O$. Consequently, the errors in the rate constants were also larger. The experiments were limited by the increasing noise at increasing concentrations of S^{IV} and by the small change in absorbance at $[S^{IV}] < 0.2$ mmol dm^{-3}. The second-order rate constants obtained at different $[H^+]$ using either S^{IV} or Tl^{III} in excess are given in Table 1.

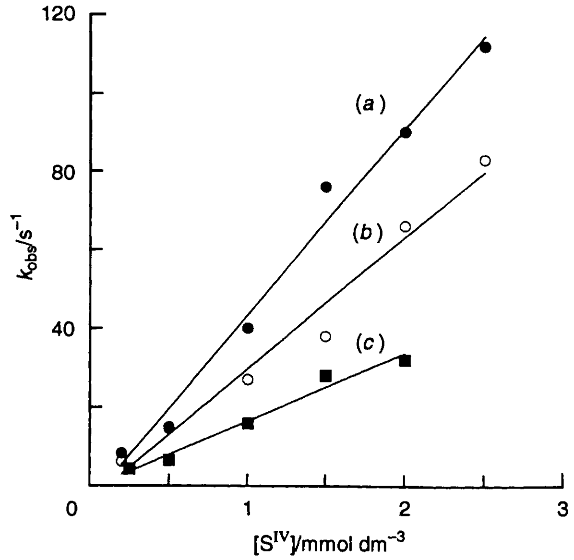


Fig. 3 Observed rate constant k_{obs} as a function of $[S^{IV}]$ and $[H^+]$. Conditions: $2.5 \times 10^{-5} < [Tl^{III}] < 2.5 \times 10^{-4}$ mol dm^{-3}, $I = 1.0$ mol dm^{-3}, 25 °C, $[H^+] = 0.6$ (*a*), 0.8 (*b*), or 1.0 mol dm^{-3} (*c*). The lines represent the best fits to the experimental data obtained by use of linear regression analysis

Table 1 Second-order rate constants defined by equation (2) at different $[H^+]$ derived from Figs. 2 and 3 using either S^{IV} or Tl^{III} in excess[a]

$[H^+]$/mol dm^{-3}	10^{-2} k/dm^3 mol^{-1} s^{-1}	Remark
0.1	4.4 ± 0.4	Excess of Tl^{III}[b]
0.2	2.0 ± 0.2	
0.4	0.86 ± 0.03	
0.6	0.51 ± 0.02	
0.8	0.36 ± 0.01	
1.0	0.29 ± 0.01	
0.6	0.47 ± 0.03	Excess of S^{IV}[c]
0.8	0.33 ± 0.03	
1.0	0.17 ± 0.02	

[a] All experiments performed at 25 °C and $I = 1.0$ mol dm^{-3}. The errors given are one standard deviation. [b] $2 \times 10^{-5} < [S^{IV}] < 1 \times 10^{-4}$ mol dm^{-3}, $0.2 < [Tl^{III}] < 7.0$ mmol dm^{-3}. [c] $0.25 < [S^{IV}] < 2.5$ mmol dm^{-3}, $2.5 \times 10^{-5} < [Tl^{III}] < 2.5 \times 10^{-4}$ mol dm^{-3}.

Discussion

Reaction Mechanism.—Reduction of thallium(III) has been shown to be first order with respect to both $[Tl^{III}]$ and $[S^{IV}]$. This indicates a simple rate law (2) where k denotes the pH-dependent second-order rate constant.

$$-d[SO_2 \cdot nH_2O]/dt = k[S^{IV}][Tl^{III}] \qquad (2)$$

The rate increases with decreasing $[H^+]$ in the interval 0.10–1.0 mol dm^{-3}, *cf.* Table 1. In general terms, redox can take place through reaction between $[Tl(H_2O)_6]^{3+}$ or $[Tl(H_2O)_5(OH)]^{2+}$ and $SO_2(aq)$ or HSO_3^-, according to any of the four reaction paths indicated in Scheme 1. Formation of outer-sphere encounter complexes between these reactants {equilibrium constant K_{os} is estimated as 20 dm^3 mol^{-1} for $[Tl(H_2O)_6]^{3+}$ and HSO_3^- and smaller for the other pairs of reactants} results in very rapid formation of inner-sphere complexes **I**–**IV**, since the thallium(III) centre is extremely substitution labile, as discussed below. The complexes **II** and **IV** are in rapid equilibrium with their deprotonated forms **II′** and **IV′**. Intramolecular, inner-sphere electron transfer within those complexes with first-order rate constants k_1–k_4, k_2' and k_4', respectively, results in formation of the final products, $[Tl(H_2O)_6]^+$ and HSO_4^-. This mechanism gives the general rate law (3), where $x_1 = k_3K_3$,

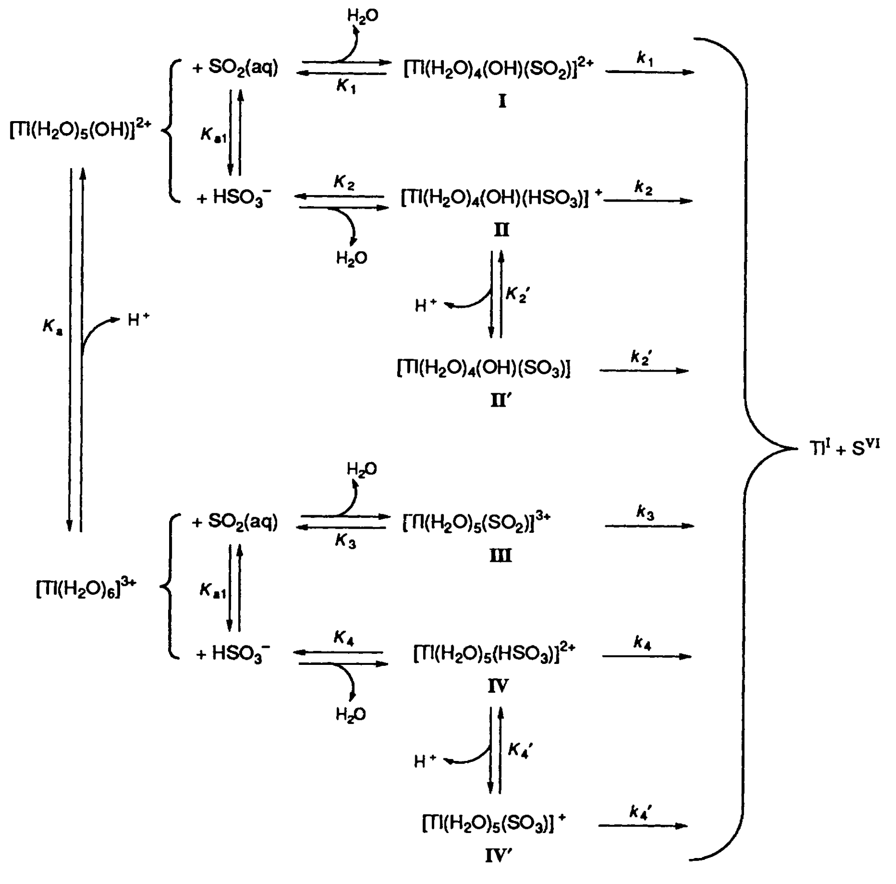
$$\frac{-d[SO_2(aq)]}{dt} = \frac{[S^{IV}][Tl^{III}]}{(K_a + [H^+])(K_{a1} + [H^+])} \times (x_1[H^+]^2 + x_2[H^+] + x_3[H^+]^{-1} + x_4) \qquad (3)$$

$x_2 = k_1K_1K_a + k_4K_4K_{a1}$, $x_3 = k_2'K_2K_2'K_aK_{a1}$ and $x_4 = k_2K_2K_aK_{a1} + k_4'K_4K_4'K_{a1}$, using the equilibrium constants defined in Scheme 1. Introduction of $K_a = 0.105$ mol dm^{-3} [39] and $K_{a1} = 0.0427$ mol dm^{-3},[39] gives $x_1 = k_3K_3$, $x_2 = 0.10k_1K_1 + 0.043k_4K_4$, $x_3 = 0.0045k_2'K_2K_2'$ and $x_4 = 0.0045k_2K_2 + 0.043k_4'K_4K_4'$. The rate law (3) is only valid provided the concentrations of the sulfito complexes are negligible in comparison with $[Tl(H_2O)_6{}^{3+}]$ and $[Tl(H_2O)_5(OH)^{2+}]$, *i.e.* the total concentration of thallium(III) is $[Tl^{III}] = [Tl(H_2O)_6{}^{3+}] + [Tl(H_2O)_5(OH)^{2+}]$. In equation (3) the total concentration of sulfur(IV) is given by $[S^{IV}] = [SO_2 \cdot nH_2O] + [HSO_3^-]$.

In order to fit the experimental pH dependence, the first and the third terms within the parentheses of equation (3) must be neglected. The stability constants K_1 and K_3 for the complexes formed with sulfur dioxide are expected to be much smaller than those for the complexes with hydrogen sulfite, K_2 and K_4. Therefore, x_1 is most likely small compared with x_2 and x_4. Also, $0.10k_1K_1 \ll 0.043k_4K_4$, so $x_2 \approx 0.043k_4K_4$.

The protolysis constant for free HSO_3^- is 5.0×10^{-7} mol dm^{-3}.[39] The corresponding protolysis constants for co-ordinated hydrogensulfite in $[Tl(H_2O)_5(HSO_3)]^{2+}$ and $[Tl(H_2O)_5(OH)(HSO_3)]^+$ are probably larger due to the influence of the charged metal centres. However, most likely, $K_2' \ll 1$ and $K_4' \ll 1$. Furthermore, $K_4' > K_2'$ due to the higher charge on the metal centre in $[Tl(H_2O)_5(HSO_3)]^{2+}$. Comparison of x_3 with x_2 shows that the neglect of the third term within the parentheses in equation (3) is also justified. To conclude, the reaction paths described by the rate constants k_2', k_1 and k_3 in Scheme 1 are negligible.

Combination of equations (2) and (3) indicates that $k(K_a + [H^+])(K_{a1} + [H^+])$ as a function of $[H^+]$ should be linear. Fig. 4 shows such a plot with use of the literature values for K_a and K_{a1}.[39] A good straight line is obtained with intercept $x_4 = 10.6 \pm 0.2$ mol dm^{-3} s^{-1} and slope $x_2 = 22.6 \pm 0.4$ s^{-1}. In this



Scheme 1

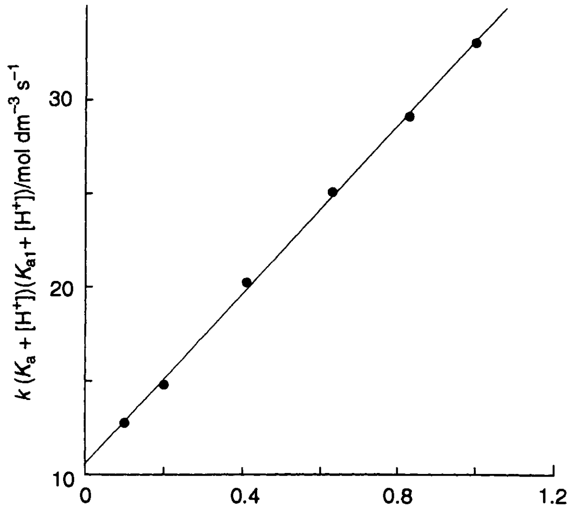


Fig. 4 The $[H^+]$ dependence of the reduction of Tl^{III}. Conditions: *cf.* Fig. 2 and Table 1 (only data for excess of Tl^{III} have been used); k denotes the second-order rate constant defined by equation (2) and calculated from the slopes of the lines in Fig. 2. The line represents the best fit of equation (3) combined with (2) to the experimental data by use of linear regression analysis

plot, $K_a = 0.105$ mol dm^{-3}, valid for 3.0 mol dm^{-3} ionic strength,[39] has been used assuming that the values are not too different at $I = 1.0$ and 3.0 mol dm^{-3}. Since $k_1K_1K_a \ll k_4K_4K_{a1}$ the value of k_4K_4 can be calculated to be 5.3×10^2 dm^3 mol^{-1} s^{-1}. An estimate of the relative values of the two terms in x_4 is more difficult since K_4' is not known.

According to the mechanism, the observed rate constant should reach a saturation value for high concentrations of sulfur(IV), if the concentrations of the sulfito complexes cannot be neglected in comparison with those of $[Tl(H_2O)_6]^{3+}$ and $[Tl(H_2O)_5(OH)]^{2+}$. Under the present experimental conditions, however, k_{obs} is a linear function of $[S^{IV}]$, *cf.* Fig. 3, which supports the assumption that the concentrations of the sulfito complexes can be neglected. Thallium(III) sulfito complexes are expected to have strong charge-transfer bands in the UV region. For example, preliminary experiments performed in this laboratory show very rapid changes in absorptivity at 245 nm after mixing hexaaquathallium(III) and thiocyanate, due to rapid complex formation. In the present system, however, the spectra give no indication of any transient high-absorbing species, further supporting the assumption of very low concentrations of sulfito complexes.

Thallium(III) is a substitution-labile metal centre. The estimated rate of water exchange for $[Tl(H_2O)_6]^{3+}$ is 3×10^8 s^{-1}.[40,41] It has been proposed that dissociation of an aqua ligand is the rate-determining step for substitution in aquathallium(III) complexes, since the rate of complex formation does not depend on the nature of the entering ligand.[42] For example, this is true for anation of $[Tl(edta)(H_2O)]^-$ (edta = ethylenediaminetetraacetate) by Cl$^-$, Br$^-$, CN$^-$ and SCN$^-$ with rate constants of *ca.* 9×10^6 dm^3 mol^{-1} s^{-1}.[42] Accordingly, substitution of an aqua ligand in the complexes $[Tl(H_2O)_6]^{3+}$ and $[Tl(H_2O)_5(OH)]^{2+}$ for SO_2 or HSO_3^- is expected to be very fast. Probably, the dissociation of the leaving ligand is rate-determining also in those cases. Since the rate constants determined in the present study are many orders of magnitude smaller than expected for substitution at Tl^{III}, rate-determining formation of sulfito complexes can be ruled out under the present experimental conditions. The absence of any indications of large concentrations of sulfito complexes must then be due to the thermodynamics, *i.e.* the complexes are so weak that their equilibrium concentrations are negligible. Early reports[43,44] on the formation of strong thallium(III) sulfito complexes refer to chloride media, where conditions are different.

Addition of SO_2 to various inert hydroxo complexes of Cr^{III}, Co^{III}, Rh^{III} and Pt^{IV} has been discussed in detail previously.[1-12,24,28] It has been shown that the hydroxide ligands react with dissolved SO_2 forming O-bonded complexes without breakage of the metal–oxygen bond. These SO_2-uptake reactions are very fast with second-order rate constants typically in the range 10^6–10^9 dm^3 mol^{-1} s^{-1}. However, due to the lability of thallium(III), formation of a sulfito complex by reaction between the hydroxide ligand of $[Tl(H_2O)_5(OH)]^{2+}$ and SO_2 is not likely in the present system.

Chain Reaction Mechanism.—In 1934 Bäckström[45] postulated a mechanism for photoinduced oxidation of sulfite by dissolved oxygen in aqueous solution. Today, the details of this chain reaction are fairly well understood. The free-radical chain oxidation proceeds *via* SO_3^-, SO_5^- and SO_4^- radicals as intermediates and is extremely effective.[33,46] The trigger of this process is the generation of sulfite radicals. As noted above, it has been suggested that metal ions as well as light may also initiate the chain by generating these radicals. Two-electron oxidants may in principle also generate sulfite radicals and thereby initiate a chain reaction. This could happen if the oxidation takes place *via* two consecutive one-electron transfers and the SO_3^- radicals have time to escape into the bulk solution and react with dissolved oxygen. However, the reaction in these systems may also proceed by a two-electron transfer process in which no observable intermediates are generated. In the present study sulfito complexes are most likely formed prior to electron transfer. The results give no information about the mechanism of electron transfer within those complexes. However, formation of SO_3^- radicals as intermediates seems unlikely. Even if the redox reaction takes place in two consecutive one-electron transfer steps the second transfer is expected to occur very rapidly within the co-ordination sphere of thallium, giving no time to release any SO_3^- radicals into the bulk solution. This is supported by the present experiments, which clearly show that the concentration of dissolved oxygen is more or less constant over a long period of time in the presence of Tl^{III} and that the concentration of S^{IV} is also constant after the direct oxidation of 1 equivalent of S^{IV} by Tl^{III}.

Acknowledgements

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