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# Kinetics of anation of Cr(III) hydrolytic oligomers: reaction of dimer with sulfate

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## Abstract

The reaction between sulfate and the Cr(III) hydrolytic dimer, $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(OH_2)_4]^{4+}$, has been followed in the pH range 3.5–4.4, [sulfate] = 0.1–0.3 M, $T = 25$ °C and $I = 1.0$ M and shown to involve two clearly separable processes: monodentate attachment of sulfate (anation) to give $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(SO_4)(OH_2)_3]^{2+}$ followed by ring closure to give a sulfato bridged dimer, $[(H_2O)_3Cr(\mu\text{-}OH)_2(\mu\text{-}SO_4)Cr(OH_2)_3]^{2+}$. Equilibrium measurements have shown that the first step is irreversible under the conditions of the kinetic measurements. Although definite conclusions about the reversibility of bridge formation could not be made this process is also likely to be irreversible. The observed rate constant for the anation process was found to be independent of [sulfate] suggesting that extensive ion-pairing occurs between the oppositely charged reactants. The rate constants for both anation and bridge formation were found to be linearly dependent on $1/[H^+]$. This is attributed to deprotonation of dimer–sulfate ion-pairs (charge 2+) and the monodentate sulfato complex (charge 2+). The linear dependence also suggests that the concentration of deprotonated species is low in the pH range 3.5–4.4. This is reasonable since $pK_{a1}$ for ions of this charge are usually greater than 5. From the kinetic data, rate accelerations of at least 30-fold have been estimated to accompany deprotonation of the reactants. They are of similar magnitude to those reported previously for other reactions involving the Cr(III) hydrolytic dimer, viz. dimerization of dimer to give tetramer and intramolecular interconversion between singly and doubly bridged dimer forms. It is concluded that deprotonated sulfato–dimer species play an important part in the tanning process since their greater reactivity in substitution processes will aid in the cross-linking of collagen.

## Introduction

In the tanning process, the animal skin is stabilised by cross-linking the polypeptide chains of collagen with complexes, or molecules, capable of acting as bridging groups. Basic Cr(III) sulfate solutions are the most widely used and most effective tanning agents, despite considerable research into the development of alternative mineral tanning agents based on salts of, for example, Zr(IV), Ti(IV) and Al(III) [1–4]. Cross-linking of collagen with Cr(III) sulfato complexes produces a material with much higher shrinkage temperatures ($T_s$) than the alternative tanning agents, an effect that can be rationalised in terms of the greater kinetic inertness of Cr(III) ($T_s$, the temperature at which the polypeptide chains in collagen collapse, is *c.* 60 °C for untanned skin, 80–95 °C for Al(III), Zr(IV) and Ti(IV) tanned skins and above 100 °C for many Cr(III) tanned products). Mixtures of salts of these metals have also been used in tanning studies [2, 5].

Despite the importance of Cr(III) sulfate solutions to the tanning industry relatively little is known about the complexes involved directly in the stabilisation of collagen. Paper electrophoresis and ion-exchange chromatography have been used to separate some of the mononuclear and polynuclear sulfato complexes present in these tanning solutions. Solution characterisation studies have shown that dimeric complexes with composition $[(H_2O)_3Cr(\mu\text{-}OH)_2(\mu\text{-}SO_4)Cr(OH)_2)_3]^{2+}$ and $[(H_2O)_4Cr(\mu\text{-}OH)(\mu\text{-}SO_4)Cr(OH_2)_4]^{3+}$ are present in these solutions [5–10] but their ability to cross-link collagen has been little explored.

Recently, we reported investigations into the tanning effectiveness of the Cr(III) hydrolytic dimer, $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(OH_2)_4]^{4+}$, and trimer, $[Cr_3(\mu\text{-}OH)_4(OH_2)_9]^{5+}$, both in the presence and absence of sulfate [1]. Sulfate was found to be beneficial in both cases yielding tanned products with $T_s \geqslant 100$ °C. Chromatographic analysis of the sulfate containing tanning solutions indicated that in the case of dimer, one product with solution properties consistent with the composition $[(H_2O)_3Cr(\mu\text{-}OH)_2(\mu\text{-}SO_4)Cr(OH_2)_3]^{2+}$ accounts for more than 95% of all chromium. Since only one major

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product is formed by the reaction of sulfate with dimer this system is attractive from the point of view of examining the kinetics of sulfate anation of the Cr(III) hydrolytic dimer aqueous solution. The results of this study are presented here.

## Experimental

### *Materials*

Salts and solutions of the hydrolytic dimer, $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(OH_2)_4]^{4+}$ [11, 12], and the dimer sulfato complex, $[(H_2O)_3Cr(\mu\text{-}OH)_2(\mu\text{-}SO_4)Cr(OH_2)_3]^{2+}$ [1], were prepared by published methods. Ion-exchange chromatography was used to purify the solutions using $Ba(ClO_4)_2$ as eluent which were then desalted by addition of $K_2SO_4$. This precipitated the $BaSO_4$ and most of the $KClO_4$. Care was taken to ensure that excess $K_2SO_4$ was not added to the dimer solution as this would then have to be taken into account in the analysis of kinetic and equilibrium data (checks for the presence of free sulfate were made by adding an aliquot of dimer solution to $Ba(ClO_4)_2$ solution). The solutions were then reduced to about one quarter of their original volume, cooled to *c.* 0 °C and filtered to remove a further precipitate of $KClO_4$. All other reagents were of analytical grade and were used without further purification. All solutions were filtered through Millipore membrane filters.

### *Instruments and methods*

UV–Vis spectra and kinetic traces were recorded on a Varian Superscan spectrophotometer whose cell compartment was maintained at 25.0 (±0.1) °C by water circulated from a water bath fitted with a Haake D8 thermostat and a Haake D12 compressor. Solution pH values were measured on a Metrohm 605 pH meter using a Ross combination glass electrode (Orion) while maintaining the temperature at 25.0 (±0.1) °C. The error in each pH reading was ±0.005 pH units. Calibrated thermometers were used to accurately measure the temperature of the reaction mixtures.

### *Kinetic measurements*

The anation of the hydrolytic dimer of Cr(III) with sulfate was followed under the following reaction conditions: pH range 3.5–4.4; [dimer] = 0.015 M (in some cases 0.03 M); [sulfate] = 0.10–0.30 M; [isonicotinamide] = 0.2 M, which acts as a buffer; $I = 1.0$ M ($NaClO_4$); $T = 25.0$ (±0.1) °C. Reaction mixtures were prepared and then adjusted to the desired pH using either NaOH or $HClO_4$ solutions (at $I = 1.0$ M) as required and the final pH value recorded. Some of this solution was immediately transferred into a spectrophotometer cell and the progress of the anation reaction followed at 417 nm (at this $\lambda$, the $\epsilon$ value for dimer in the presence of excess sulfate was $20.1 \pm 0.1$ $M^{-1}$ $cm^{-1}$ and was independent of [sulfate]). After a small initial increase, a drop in absorbance of up to 0.1 units was observed as the reaction proceeded. The UV–Vis spectrum of pure solutions of the dimer sulfate complex formed in this reaction and purified by cation exchange chromatography showed maxima at 581 ($\epsilon = 16.7$ $M^{-1}$ $cm^{-1}$ per Cr) and 417 ($\epsilon = 17.7$ $M^{-1}$ $cm^{-1}$ per Cr) nm which compared well with literature reports for $[(H_2O)_3Cr(\mu\text{-}OH)_2(\mu\text{-}SO_4)Cr(OH_2)_3]^{2+}$ [7]. At the wavelength of the kinetic runs (417 nm), the average of the molar extinction coefficients determined at the end of each kinetic run was $18.2 \pm 0.4$ $M^{-1}$ $cm^{-1}$ per Cr. The charge and sulfate/Cr ratio for the product of kinetic runs were confirmed to correspond to those reported recently for this complex [1]. Thus, the dimer sulfate complex was confirmed to be the only significant product of the anation reaction.

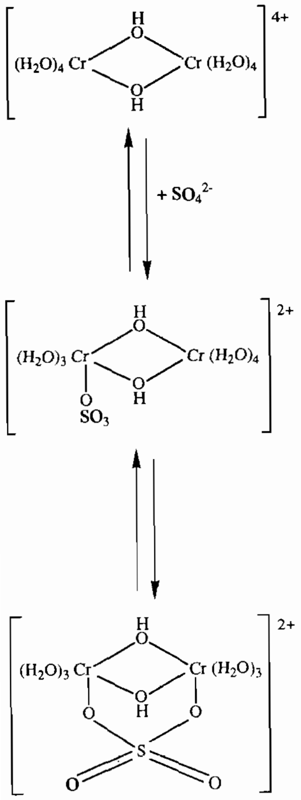
### *Equilibrium measurements*

Solutions of the dimer–sulfate complex were equilibrated for several days at various pH values in the range 3.5–4.4, $T = 25$ °C, $I = 1.0$ M and with isonicotinamide (0.2 M) as buffering agent. Spectrophotometric and chromatographic checks were used to ensure that equilibrium had been reached. A known volume of this solution was then analysed for chromium spectrophotometrically following conversion to $CrO_4^{2-}$ [12]. Another sample was diluted by ten-fold with ice-cold $HClO_4$ (0.002 M) and adsorbed onto a jacketed Sephadex SP C25 ion-exchange column. The column was maintained below 5 °C by circulating cold propanol through the jacket to reduce the rate of hydrolytic reactions. The column was washed thoroughly with ice-cold perchloric acid solution (pH 3) and the Cr(III) species that were present eluted with 1 M $NaClO_4$ solution, also at pH 3. The dimer sulfate complex eluted first as a clearly separated fraction followed by the hydrolytic dimer. Each of these fractions were collected separately and analysed for Cr. Small amounts of tetramer and higher oligomers which eluted after dimer were collected as one fraction and analysed for Cr. This occurs because at the pH values of the equilibrium studies the hydrolytic dimer, formed by release of sulfate from the sulfato dimer, can polymerize to give higher oligomers. In contrast, little formation of other oligomers was evident in kinetic studies of the reaction of dimer with sulfate because the monosulfato complex, $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(SO_4)(OH_2)_3]^{2+}$, formed relatively rapidly (see 'Results and discussion'). In all cases the recovery of Cr was quantitative. The [sulfate] released during the equilibration process, i.e. the concentration of unbound sulfate present at equilibrium, was determined as the difference between the initial and final equilibrium concentration of dimer sulfate complex. The calculation of equilibrium constants is described in the following section.

## Results and discussion

### *Kinetic measurements*

The rate of reaction between sulfate and the hydrolytic dimer of Cr(III) was measured in the pH range 3.5–4.4. The reaction was monitored at 417 nm where incorporation of sulfate into the dimer results initially in a slight increase in absorbance followed by a drop of up to 0.1 units for a [dimer] ~0.015 M (see Fig. 1). Taking account of previous work on sulfato complexes this observation can be accounted for in terms of the two consecutive reactions shown in Scheme 1. The product of the first step could not be identified but it is most likely a dimer complex with a monodentate sulfate attached to one Cr(III) centre. This is a reasonable proposal since the initial increase in absorbance mirrors that observed in the reaction of $Cr^{3+}$ with sulfate to give $[(H_2O)_5CrSO_4]^+$ [7, 14]. The molar extinction coefficient for the monosulfato dimer complex, $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(SO_4)(OH_2)_3]^{2+}$, at 417 nm calculated from the absorbance changes ($\epsilon = 21 \pm 0.6$ $M^{-1}$ $cm^{-1}$ per Cr) and as part of the analysis of the kinetic data ($\epsilon = 20.4 \pm 0.3$ $M^{-1}$ $cm^{-1}$ per Cr) compares extremely well with that for $[(H_2O)_5CrSO_4]^+$ ($\lambda_{max} = 418$ nm, $\epsilon = 20.7$ $M^{-1}$ $cm^{-1}$ per Cr) [14]. The second step results in formation of the dimer sulfato complex, $[(H_2O)_3Cr(\mu\text{-}OH)_2(\mu\text{-}SO_4)Cr(OH_2)_3]^{2+}$, which has been previously characterised [1] and shown to be present in Cr(III) tanning solutions [6–9]. The molar extinction coefficient of this species at 417 nm determined at the end of each kinetic run ($\epsilon = 18.2 \pm 0.4$ $M^{-1}$ $cm^{-1}$ per Cr) compares extremely well with that of pure solutions of $[(H_2O)_3Cr(\mu\text{-}OH)_2(\mu\text{-}SO_4)Cr(OH_2)_3]^{2+}$ ($\epsilon = 17.7 \pm 0.2$ $M^{-1}$ $cm^{-1}$ per Cr). Solution studies have concluded that, in this and related binuclear sulfato complexes of Cr(III), the sulfate group adopts a bridging mode in preference to chelation [6, 7, 13]. Solid state data also indicates that monodentate and bridging coordination modes are more common [15–17]. For the first transition series, $[(trpn)Co(\eta^2\text{-}SO_4)]^+$ is one of very few complexes to be structurally characterised which contains a chelating sulfate [18]. This coordination mode appears to be more common for elements of the second and third series.



Scheme 1. Two-step anation of the Cr(III) hydrolytic dimer.

Fitting of the absorbance versus time data to the equation for a first order process led to systematic deviations in the initial stages of the reaction. Since the data suggested the existence of two steps, it was fitted to the expression for two consecutive first order processes (eqn. (1)) using non-linear least-squares analysis:

$$A_t = B\exp(-k_{obs\,1}t) + C\exp(-k_{obs\,2}t) + D \qquad (1)$$

The rate of the first step was sufficiently faster than the second (about 3–4 fold faster) to allow numerical solutions to be obtained without convergence problems. The coefficients $B$ and $C$ were refined as part of the computer based fitting of the data and, together with spectrophotometrically determined $\epsilon$ values for dimer and the dimer sulfate complex, used to establish the $\epsilon$ value for the intermediate discussed above. The parameter $D$, which corresponds to the absorbance at the end of the reaction (usually taken after 10 half-lives), was either refined as part of the fitting procedure or determined from kinetic traces. The two methods gave the same values of the rate constants, $B$ and $C$. Figure 1 shows a typical plot of the experimental data and calculated curve which highlights the excellent fits that were obtained using eqn. (1). This was further demonstrated by the fact that the deviations between calculated and measured $A_t$ were random over more than five half-lives of the reaction.

At each pH value, rate constants were determined over a range of [sulfate] (0.1–0.3 M). This showed that both the observed rate constants ($k_{obs\,1}$ and $k_{obs\,2}$) were independent of [sulfate] (see footnotes to Table 1). The values of $k_{obs\,1}$ and $k_{obs\,2}$ obtained at each pH were averaged and are listed in Table 1. The errors in each

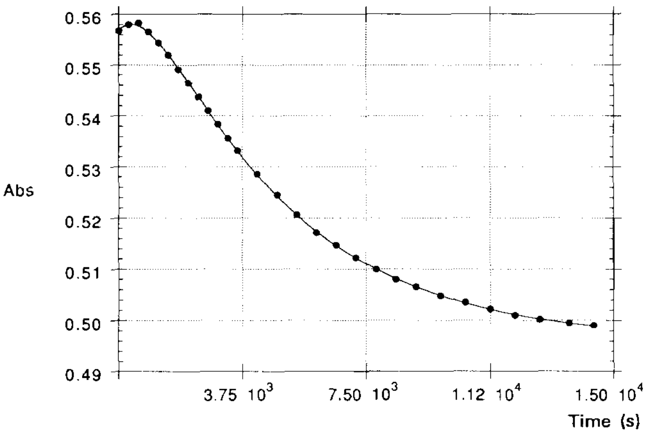


Fig. 1. A typical plot showing the change in absorbance with time observed for the reaction of sulfate with the Cr(III) hydrolytic dimer (reaction conditions were pH = 3.50, [sulfate] = 0.200 M, [dimer] = 0.015 M). The solid line represents fitted curve obtained by least-squares fitting of the data to eqn. (1), the final parameters were $B = 0.5568$, $C = 0.5837$, $D = 0.4959$, $k_{obs\,1} = 10.4 \times 10^{-4}$ s$^{-1}$ and $k_{obs\,2} = 2.33 \times 10^{-4}$ s$^{-1}$.

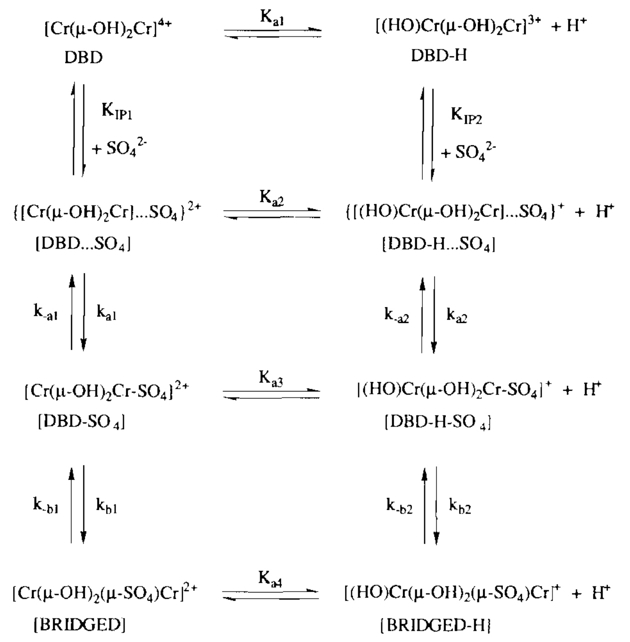
TABLE 1. Observed rate constants for the two-step reaction of sulfate with the Cr(III) hydrolytic dimer, [sulfate] = 0.1–0.3 M, 25 °C and $I = 1.0$ M

| pH | $10^4 \times k_{obs\,1}$ (s$^{-1}$) | $10^4 \times k_{obs\,2}$ (s$^{-1}$) |
|---|---|---|
| 3.50 | 9.9 (±1.5) | 2.52 (±0.25) |
| 3.60 | 9.8 (±1.0) | 3.72 (±0.35) |
| 3.70 | 12.4 (±1.6) | 3.72 (±0.10) |
| 3.88 | 13.3 (±2.7) | 4.62 (±0.50) |
| 4.00 | 30.7 (±4.2) | 6.12 (±0.53) |
| 4.10 | 28.1 (±3.2) | 8.63 (±0.47) |
| 4.20 | 28.8 (±1.8)[a] | 9.28 (±0.90)[a] |
| 4.30 | 39.5 (±4.0) | 13.10 (±0.52) |
| 4.40 | 48.0 (±4.8) | 14.41 (±0.88) |

[a] Typical variation in rate constants with [sulfate] at pH = 4.20 were as follows {in the format, [sulfate] (M), $10^4 \times k_{obs\,1}$ (s$^{-1}$), $10^4 \times k_{obs\,2}$ (s$^{-1}$)}: 0.100, 27.2, 7.67; 0.150, 30.3, 9.85; 0.200, 26.8, 8.93; 0.300, 31.0, 9.98. These values were averaged to give the rate constants listed in the table. No systematic variations in rate constants were found at the pHs of this study.

rate constant are larger than might be expected for this type of kinetic data. This is probably a reflection of the relatively small absorbance changes that the overall reaction produces, which is particularly small for the first step and at the lower pH, as well as errors associated with the setting and measurements of pH values.

The two-step anation of dimer can be rationalised in terms of the reaction pathways outlined in Schemes 1 and 2. The observed changes in absorbance, and molar extinction coefficients determined from them, are consistent with the proposal that $k_{obs\,1}$ is a measure of the rate of attachment of sulfate to the dimer to give $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(SO_4)(OH_2)_3]^{2+}$ and that $k_{obs\,2}$ is the rate of ring closure within this species to give $[(H_2O)_3Cr(\mu\text{-}OH)_2(\mu\text{-}SO_4)Cr(OH_2)_3]^{2+}$. The invariance of the observed rate constants with [dimer] and [sulfate] suggests the presence of extensive ion-pairing (Scheme 2) between the reactants which are of high and opposite charge. The Fuoss and Davies equations [19] predict an ion-pairing constant of 1700 M$^{-1}$ between species of charge +4 and −2, and 200 M$^{-1}$ between species of charge +3 and −2. The real constant may be even greater since this expression does not account for H-bonding effects. The existence of ion-pairing interactions between dimer and sulfate is not unexpected since earlier work on the sulfate anation of $Cr^{3+}$ had found that the rate constants were virtually independent of [sulfate] and [$Cr^{3+}$] over a wide range of reaction conditions [14].



Scheme 2. Mechanism of sulfate anation of the Cr(III) hydrolytic dimer.

The linear dependence of the observed rate constants ($k_{obs\,1}$ and $k_{obs\,2}$) on the inverse of the acid concentration (Figs. 2 and 3) can be interpreted in terms of reaction pathways involving fully protonated and monodeprotonated forms of dimer (Scheme 2). The first step involving formation of the monodentate sulfato complex is irreversible since equilibrium data indicate that even under the least favourable conditions of high pH and low [sulfate] (see Table 2), less than 3.5% of free hydrolytic dimer would be present at equilibrium. Taking this factor into account and given that the reaction rate is independent of [sulfate] and [dimer] (i.e. the concentration of free dimer is small), the reaction rate law is of the form:

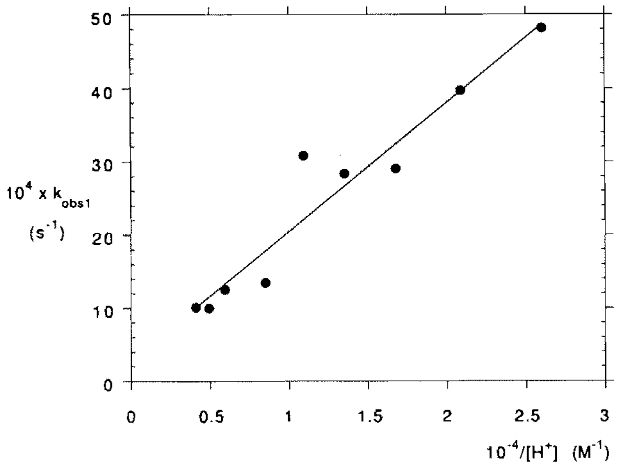


Fig. 2. Inverse acid dependence of the observed rate constant ($k_{obs\,1}$) for the faster first step in the reaction of sulfate with the Cr(III) hydrolytic dimer (fitted line = solid line).

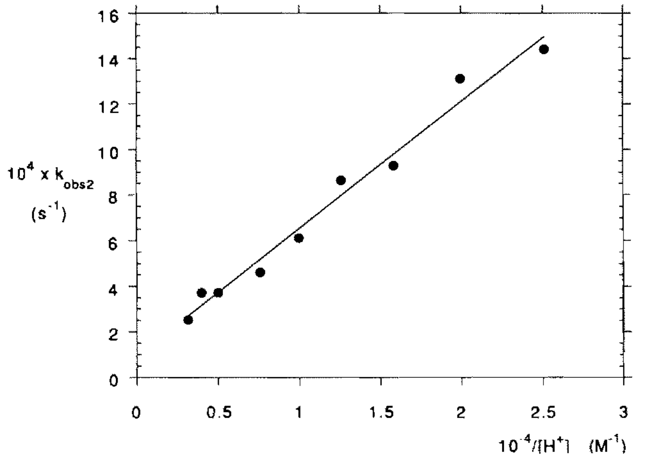


Fig. 3. Inverse acid dependence of the observed rate constant ($k_{obs\,2}$) for the slower second step in the reaction of sulfate with the Cr(III) hydrolytic dimer (fitted line = solid line).

$$\frac{d[\text{DBD–SO}_4]}{dt} = \{k_{a1}[\text{DBD}\ldots\text{SO}_4]+k_{a2}[\text{DBD-H}\ldots\text{SO}_4]\} \qquad (2)$$

In eqn. (2), $[\text{DBD}\ldots\text{SO}_4]$, $[\text{DBD-H}\ldots\text{SO}_4]$ are the concentrations of dimer sulfate ion-pairs and mono-deprotonated dimer and sulfate ion-pairs while $k_{a1}$ and $k_{a2}$ are the rates of sulfate attachment within these ion-pairs. Rearrangement of eqn. (2) gives:

$$\frac{d[\text{DBD–SO}_4]}{dt} = \left\{\frac{[k_{a1}+k_{a2}K_{a2}/[\text{H}^+]]}{[1+K_{a2}/[\text{H}^+]]}\right\}[\text{DBD}\ldots\text{SO}_4]_\text{T} \qquad (3)$$

where $[\text{DBD}\ldots\text{SO}_4]_\text{T}$ and $K_{a2}$ are the total concentration of dimer sulfate ion-pairs (which also equals $[\text{dimer}]_\text{init}$) and the first acid dissociation constant of the $[\text{DBD}\ldots\text{SO}_4]^{2+}$ ion-pair. Since in addition to being independent of [reactants], $k_{obs\,1}$ increases linearly with $1/[\text{H}^+]$, the $K_{a2}/[\text{H}^+]$ term present in the denominator is small and has no effect on $k_{obs\,1}$. This is reasonable since $K_{a2}$ for the $[\text{DBD}\ldots\text{SO}_4]^{2+}$ ion-pair would be expected to be significantly smaller than $K_{a1}$ for free dimer ($pK_{a1}=3.68$) and little deprotonation is anticipated in the pH range 3.5–4.5. Thus, $k_{obs\,1}$ simplifies to:

$$k_{obs\,1} = \left\{k_{a1} + \frac{k_{a2}K_{a2}}{[\text{H}^+]}\right\} \qquad (4)$$

Weighted linear least-squares analysis gave a slope of $1.717(\pm 0.024)\times 10^{-7}$ $M^{-1}$ $s^{-1}$ which corresponds to $k_{a2}K_{a2}$ and intercept of $3.48(\pm 0.20)\times 10^{-4}$ $s^{-1}$ which corresponds to $k_{a1}$.

The slower step, which converts the monodentate sulfate into a bridging sulfate, is probably irreversible but this is difficult to establish experimentally because the two species are of the same charge and cannot be separated using, for example, ion-exchange chromatography. Indirect evidence in favour of an irreversible process comes from the observation that the spectrum of the final product does not vary with pH over the range used in this study and it is also the same as that measured in more acidic solutions (pH 2). Such changes in pH usually give rise to major differences in the equilibrium distribution of hydrolytic species. Nevertheless, for the purposes of the discussion to follow a reversible process will be assumed in the development of the rate equation. The rate law may be written as:

$$\frac{d[\text{BRIDGED}]}{dt} = \left\{\begin{matrix} k_{b1}[\text{DBD–SO}_4]+k_{b2}[\text{DBD-H–SO}_4] \\ -[k_{-b1}[\text{BRIDGED}]+k_{-b2}[\text{BRIDGED-H}]]\end{matrix}\right\} \qquad (5)$$

In eqn. (5), [BRIDGED] and [BRIDGED-H] are the concentrations of the protonated and mono-deprotonated bridged dimer sulfate complex, respectively, $k_{b1}$ and $k_{b2}$ are the rates of formation of the bridged complex from monodentate sulfate complexes and $k_{-b1}$ and $k_{-b2}$ are the rate constants for the reverse reactions. From this equation the following expression for $k_{obs\,2}$ is obtained:

$$k_{obs\,2} = \left[\frac{k_{b1}+k_{b2}K_{a3}/[\text{H}^+]}{1+K_{a3}/[\text{H}^+]}\right] + \left[\frac{k_{-b1}+k_{-b2}K_{a4}/[\text{H}^+]}{1+K_{a4}/[\text{H}^+]}\right] \qquad (6)$$

In eqn. (6), $K_{a3}$ and $K_{a4}$ are the acid dissociation constants of the monodentate sulfato complex

(DBD–$SO_4$) and the bridged sulfato complex (BRIDGED). Since $k_{obs\,2}$ varies linearly with $1/[H^+]$ it can be concluded that the acid dependent terms in the denominator are small. Both $K_{a3}$ and $K_{a4}$ are expected to be smaller than $K_{a1}$ for the dimer ($pK_{a1}=3.68$, charge +4) because of the lower charge of these complexes (+2). Thus, $k_{obs\,2}$ is given by:

$$k_{obs\,2}=[k_{b1}+k_{-b1}]+[k_{b2}K_{a3}+k_{-b2}K_{a4}]/[H^+] \qquad (7)$$

Weighted least-squares fitting of the data to eqn. (7) gave a slope of $5.83(\pm0.07)\times10^{-8}$ $M^{-1}$ $s^{-1}$ and intercept of $8.00(\pm0.43)\times10^{-5}$ $s^{-1}$.

### *Equilibrium measurements*

Solutions of the previously characterised dimer–sulfate complex [1] were used in equilibration experiments conducted in the pH range 3.5–4.4. This method was found to be most convenient not only because the Cr(III) species present in the equilibrium mixtures could be separated by ion-exchange chromatography, and their concentrations determined following spectrophotometric analysis as chromate, but also because the concentration of unbound sulfate could be easily determined. Apparent equilibrium constants ($K_{APP}$) were then calculated using the expression:

$$K_{APP}=\frac{[DIM\text{–}SO_4]_T}{[DBD]_T[SO_4{}^{2-}]_T} \qquad (8)$$

The bridged and monodentate sulfate dimers (assuming this is present) are of the same charge and cannot be satisfactorily separated using ion-exchange chromatography. This means that $[DIM\text{–}SO_4]_T$ is the sum of $[DBD\text{–}SO_4]_T$ and $[BRIDGED]_T$. The $[SO_4{}^{2-}]_T$ was taken as the difference between initial and equilibrium $[DIM\text{–}SO_4]_T$ and thus takes into consideration any polymerization of the hydrolytic dimer which may have occurred during the equilibration period. It is the sum of the concentrations of [DBD...$SO_4$], [DBD-H...$SO_4$] and $[SO_4{}^{2-}]_{free}$ while $[DBD]_T$ is comprised of the concentrations of [DBD], [DBD-H], [DBD...$SO_4$] and [DBD-H...$SO_4$]. The acid dependence of $K_{APP}$ is summarised in Table 2 and Fig. 4. Even with the rate data that has been obtained for this system it is not possible to extract equilibrium constants for individual steps in the anation reaction. The main reason for this is that the determination of the acid dissociation constants for dimer sulfate ion-pairs and dimer sulfate complex will require measurement at pH>5 (the $pK_a$s for these species will be greater than 5) where hydroxide precipitates will form. Nevertheless, Fig. 3 clearly shows a clear increase in $K_{APP}$ with increasing acid concentration. This means that the sulfato dimer complexes are less stable as pH increases.

TABLE 2. Apparent equilibrium constants for the reaction of sulfate with the Cr(III) hydrolytic dimer with sulfate at 25 °C and $I=1.0$ M

| pH | $K_{APP}$ ($M^{-1}$)[a] |
|---|---|
| 3.50 | 640 |
| 3.59 | 610 |
| 3.60 | 720 |
| 3.70 | 550 |
| 3.80 | 450 |
| 3.89 | 410 |
| 4.00 | 420 |
| 4.11 | 360 |
| 4.20 | 270 |
| 4.30 | 280 |

[a] $K_{APP}$ is defined in the text.

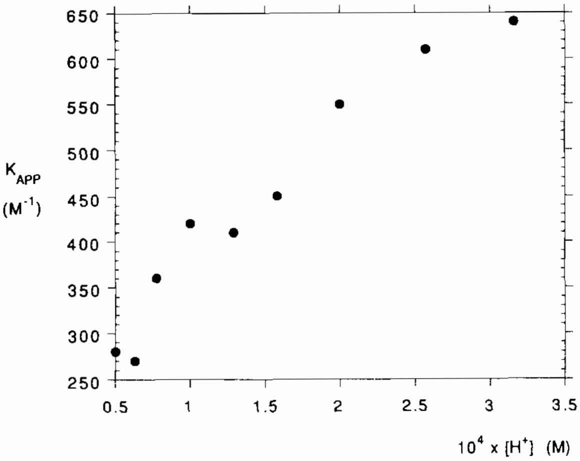


Fig. 4. Acid dependence of the apparent equilibrium constant ($K_{APP}$) for the reaction of sulfate with the Cr(III) hydrolytic dimer.

### *Interpretation of rate and equilibrium constants*

Rate enhancements attributable to deprotonation of the metal ion are a common feature of the substitution reactions at $Cr^{3+}$. An extensive series of anation reactions of $Cr^{3+}$ with rate accelerations of up to 5000-fold have been reported and the rate of water exchange on $CrOH^{2+}$ is 75 times faster than on $Cr^{3+}$ [20]. Deprotonation has also been found to accelerate hydrolytic polymerisation reactions. The rate of dimerisation of mononuclear Cr(III) species was found to increase by 50–200-fold with each deprotonation of $Cr^{3+}$, viz. the reaction of $CrOH^{2+}$ with $Cr(OH)_2{}^+$ is 200 times faster than the reaction between $CrOH^{2+}$ and $CrOH^{2+}$ [21]. More recently, we reported rate accelerations of 25–160-fold for the conversion of the hydrolytic dimer into tetramer [22]. This study confirms the existence of such effects in the anation reactions of hydrolytic oligomers of Cr(III).

Although $pK_a$s for $[DBD...SO_4]^{2+}$, $[DBD\text{–}SO_4]^{2+}$ and $[BRIDGED]^{2+}$ cannot be determined experimentally they are expected to be greater than the $pK_{a1}$ value for the dimer of 3.68. Assuming $pK_{a1} \sim 5$ for $[DBD...SO_4]^{2+}$ ($pK_{a1}$ would have to be at least 5 since the rate data suggests that in the pH range of this study the concentration of $[DBD\text{-}H...SO_4]^{+}$ is small) and dividing the rate constant for the acid dependent pathway ($k_{a2}K_{a2} = 1.717(\pm 0.024) \times 10^{-7}$ $M^{-1}$ $s^{-1}$) by this value gives $k_{a2} = 1.72 \times 10^{-2}$ $s^{-1}$. Comparing this rate constant with $k_{a1} = 3.48(\pm 0.20) \times 10^{-4}$ $s^{-1}$, an acceleration of at least 30-fold is found to result from deprotonation of $[DBD...SO_4]^{2+}$. Similar comparisons for the ring closure reactions involved in the formation of the sulfato bridged dimer would be possible if $k_{b1}$, $k_{-b1}$, $k_{b2}$ and $k_{-b2}$ were known. An indication of the magnitude of the rate enhancement caused by deprotonation can be obtained by assuming that $k_{b1} > k_{-b1}$ and $k_{b2} > k_{-b2}$ (circumstantial evidence in favour of this was given earlier) and $pK_{a3}$ and $pK_{a4}$ about 5. Applying this assumption to the acid independent term, gives $k_{b1} = 8.00 \times 10^{-5}$ $s^{-1}$ while from the acid dependent term $k_{b2} = 5.8 \times 10^{-3}$ $s^{-1}$ is obtained. Thus, a rate increase of more than 70-fold results from deprotonation of $[DBD\text{–}SO_4]^{2+}$. A similar rate enhancement is obtained if it is assumed that the bridge formation reactions occur at about the same rate as bridge cleavage (i.e. $k_{b1} \sim k_{-b1}$ and $k_{b2} \sim k_{-b2}$). It should be noted that these comparisons are based on high estimates of acid dissociation constants, $K_{a2}$, $K_{a3}$ and $K_{a4}$, and that in reality the acceleration in rates resulting from deprotonation could be an order of magnitude larger.

The increase in rate of sulfate anation of the Cr(III) hydrolytic dimer of greater than 30-fold that occurs on deprotonation of the dimer can be interpreted in terms of labilisation of the Cr(III) coordination sphere. Since the observed rate constants were independent of [sulfate], ion-pairing effects could be separated from kinetic effects. Thus, this rate acceleration is a direct measure of degree of labilisation of the primary coordination sphere of the Cr(III) dimer that results from deprotonation. It is interesting to note that this rate enhancement is of the same magnitude at those observed in the dimerisation of dimer to give tetramer [22]. The fact that the sulfate ring closure process occurs more rapidly through the mono-deprotonated form of $[(H_2O)_4Cr(\mu\text{-}OH)_2Cr(SO_4)(OH_2)_3]^{2+}$ ($[DBD\text{-}H\text{-}SO_4]^{2+}$) suggests that this type of process is also enhanced by deprotonation. A similar effect has been reported for the intramolecular rearrangement of the Cr(III) hydrolytic dimer where it was found that the conversion of mono-hydroxy bridged dimer into dihydroxy bridged dimer occurs more rapidly through mono- and doubly-deprotonated forms of singly bridged dimer [23]. In this case, the first deprotonation process generates a coordinated $OH^-$, which is a better nucleophile for effecting ring closure, the second deprotonation process causes a larger increase in rate attributable to labilisation of the Cr(III) coordination sphere. In this same work, the rate of cleavage of mono-deprotonated DBD to singly bridged dimer (SBD-2H) was shown to be faster than for the fully protonated DBD [23, 24]. This suggests that in the case of the reaction of dimer with sulfate both the anation and aquation reactions will be faster for the mono-deprotonated reactants. The fact that $K_{APP}$ decreases with pH suggests that deprotonation causes a greater increase in the rate of the aquation reaction compared with the rate of the anation reaction.

In previous work, we have shown that the dimer sulfate complex is an efficient tanning agent [1]. The rate and equilibrium constants for the reaction of dimer with sulfate provide further rationalisation for the conditions that are generally used in the tanning process and which have been established by empirical methods. As indicated in the introduction, tanning generally involves penetration of the hide or collagen source by the Cr(III) sulfate complex followed by reaction with collagen to cross-link the polypeptide chains. Penetration is generally carried out at low pH (~2) primarily to ensure that the carboxyl groups are fully protonated and do not react with Cr(III) species before an even distribution of Cr(III) can be achieved. The pH is then raised to between 4 and 4.5 to allow deprotonation of the carboxylic acids and binding of these groups to Cr(III). While it is correct to suggest that the binding properties of carboxylic groups are improved on deprotonation, other important factors need to be considered. We have concluded here than even at pHs as low as 4, small amounts of deprotonated dimeric Cr(III) sulfato species greatly affect the rate of substitution processes. The higher reactivity of this species, which has been shown to be present in tanning solutions, would certainly contribute to the observed faster rate of reaction between carboxylates and Cr(III) species under the conditions of tanning. In addition, $K_{APP}$ for the dimer sulfate complex used in this study decreases with pH indicating that there is a relative increase in the stability of hydrolytic dimer forms. This may be important in tanning since the breakdown of the dimer sulfate complex, involving the release of sulfate, could be assisted by the formation of stable linkages through nucleophilic attack of groups such as carboxylates groups present on collagen.

Extensive studies by Matijevic and co-workers [25] have shown that hydrolysis of dimer sulfate solutions produces chromium hydroxide sols of narrow size distribution. The results we have presented here suggest that the slow and controlled release of sulfate, such as is likely to occur when solutions of the dimer sulfate complex are aged in the pH range 4–5, and subsequent slow polymerization could be vital processes in the production of these sols.

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