Inorganica Chimica Acta, 36 (1979) 55–61
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Acid Hydrolysis of Tris(salicylaldehydato)chromium(III): Kinetics and Anion Catalysis

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Received November 17, 1978

The acid hydrolysis of the title complex $[Cr(SA)_3]$ *can be described as a sequence of three consecutive steps according to (1) with* $k^I > k^{II} > k^{III}$:

$$\underset{\text{I}}{[Cr(SA)_3]} \xrightarrow{k^I} \underset{\text{II}}{[Cr(SA)_2]^+} \xrightarrow{k^{II}} \underset{\text{III}}{[Cr(SA)]^{2+}} \xrightarrow{k^{III}} \underset{\text{IV}}{Cr^{3+}} \quad (1)$$

The intermediates II *and* III *were separated and characterized.*

The rate law for the hydrolysis of I, II *and* III *in perchloric acid is 1st order in complex with* $k_{obs} = k_0 + k[H^+]$. *While the hydrolysis of* I *is not affected by the type of anion present the acid dependent paths of* II → III *and of* III → IV *are anion catalysed, especially by oxo anions such as nitrate and sulfate (*cis*-effect).*

The rate law describing the acceleration effect of various anions is presented and mechanistically interpreted. The results of independent anation studies with IV *support the interpretation of inner sphere displacement of water by the oxo anion as being rate determining (*I_a*-mechanism).*

Introduction

As has been shown previously [1], the acid hydrolysis of $[Cr(SA)_3]$ (= tris(salicylaldehydato)-chromium(III)) takes place stepwise and can be described as a sequence of 3 pseudo first order consecutive reactions (hydration of the charged species omitted):

$$\underset{I}{[Cr(SA)_3]} \xrightarrow{k^{I}} \underset{II}{[Cr(SA)_2]^+} \xrightarrow{k^{II}} \underset{III}{[Cr(SA)]^{2+}} \xrightarrow{k^{III}} \underset{IV}{Cr^{3+}} \quad (1)$$

The intermediates *II* and *III* were separated and characterized [2]. Separate studies on their hydrolysis confirmed the results of the overall reaction [1], *i.e.*, $k^{I} > k^{II} > k^{III}$. Furthermore, it was found that for the hydrolysis of *III* there is an acid independent as well as an acid dependent pathway [2].

It has been observed that the rate of substitution in chromium(III) complexes like $[Cr(H_2O)_5X]^{2+}$ (X = halogen, pseudohalogen, NH_3, H_2O) and $[Cr(NH_3)_n(H_2O)_{6-n}]^{3+}$ is enhanced by addition of oxo anions such as nitrate [3–8], nitrite [6, 9], carbonate [6], sulfate [4, 6], sulfite [5, 6, 10], and carboxylate [6, 11]. This acceleration has been ascribed to a specific '*cis*-effect' of the potentially bidentate oxo anions [5, 6].

Our recent studies on the hydrolysis of the species $[Cr(SA)]^{2+}$ revealed that the aquation of this cationic chelate complex is also catalysed by oxo anions, but obviously only through the acid dependent pathway [12].

The present study was undertaken (i) to complete the information on the pH and oxo anion dependence of the various steps in scheme (1), (ii) to correlate proton and anion effects with the properties of the chromium species involved and (iii) to compare the kinetics of the anation reaction between *IV* and sulfate anions with those of the sulfate catalysed acid hydrolysis of *III*.

Experimental

Tris(salicylaldehydato)chromium(III) = $[Cr(SA)_3]$ = I

1.88 g $[Cr(THF)_3Cl_3]$ (= 5 mmol), prepared according to a standard procedure [13], and 2.44 g salicylaldehyde (= 20 mmol) were dissolved in 50 ml EtOH. After addition of 2.72 g $NaAc \cdot 3H_2O$ (= 20 mmol) the solution was refluxed for 1 h. The sodium chloride generated during the reaction was separated by filtration of the hot solution. Upon cooling the brown complex precipitated in a micro crystalline form. Yield: 1.2 g *I* (= 58%). Analysis (calculated values in brackets): C = 60.38 (60.73), H = 3.61 (3.64) Cr = 12.45 (12.52) %.

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The melting point of 222–223 °C was slightly higher than the previously published value of 215–216 °C [14].

Di-aqua-bis(salicylaldehydato)chromium(III) Cation = $[Cr(SA)_2(H_2O)_2]^+$ = II

A saturated solution of *I* in 100 ml of 1 N $HClO_4$/EtOH (1:1) was heated to 40 °C for 2 h to obtain the maximum concentration of *II*. The various hydrolysis products present in the yellow solution were separated by cation exchange (SP-Sephadex C-25; 2.3 ± 0.3 meq/g; Pharmacia Fine Chemicals, Uppsala, Sweden) in a column (length 25 cm, diameter 2 cm) cooled to 0 °C. Elution with 0.1 N $HClO_4$ at a rate of 2 ml/min led to the separation of a yellow fraction for which the ratio Cr:SA = 1:(2.01 ± 0.1) was found by application of an analytical procedure described previously [1].

Tetra-aqua-mono(salicylaldehydato)chromium(III) Cation = $[Cr(SA)(H_2O)_4]^{2+}$ = III

A saturated solution of *I* in 100 ml of 1 N $HClO_4$/EtOH (1:1) was heated to 40 °C for 12 h. The separation of *III* was also done by cation exchange (application of the same resin as described above). The fraction obtained upon elution with 0.5 N $HClO_4$ was found to have a mole ratio of Cr:SA = 1:(0.97 ± 0.04).

Hexa-aqua-chromium(III) Perchlorate = $[Cr(H_2O)_6](ClO_4)_3$

This compound was prepared according to a procedure published elsewhere [15].

Sulfato-penta-aqua-chromium(III) Cation = $[Cr(H_2O)_5SO_4]^+$ = V

This cation was prepared as described elsewhere [16]. The separation by cation exchange (resin: LEWATIT, SP 1800, 100–200 mesh ASTM; column: length 30 cm, diameter 2 cm; elution with 2 N $HClO_4$ at 4 ml/min) led to a mol ratio Cr:SO_4^{2-} = 1:(1.04 ± 0.06).

VIS Spectra

All spectra were taken with a ZEISS (DMR22) or UNICAM (SP1800) spectrophotometer.

At 20–25 °C the following data were recorded:

compound	solvent	λ_{max}(nm)	$\epsilon_{max}(M^{-1}\ cm^{-1})$
I	2 N $HClO_4$/ EtOH (1:1)	413	8100 ± 100
II	1 N $HClO_4$	408	5300 ± 100
III	1 N $HClO_4$	405	2700 ± 60

Kinetic Measurements

The acid hydrolysis of *II* and *III* was studied at $[HClO_4]$ = 0.1–3 N and at I = 3($NaClO_4$). For solubility reasons a mixture of $HClO_4$/EtOH (1:1) was used for *I* with $[HClO_4]$ = 0.1–1.0 N and I = 1.0($NaClO_4$).

Anion catalysis was investigated by addition of appropriate solutions of NaCl, NaBr, $NaNO_3$, and $NaHSO_4$.

The anation of *IV* to *V* was followed at I = 3($NaClO_4$), $[HClO_4]$ = 1.0, and $[NaHSO_4]_0$ = 0.1–1.5 *M*.

The spectrophotometric measurements were made repetitively while the solutions under study remained in the thermostated quartz cells for the whole run (no sampling). The temperature in the cells was measured with a thermocouple.

The determination of k_{obs} for the various steps of hydrolysis from absorbance data was described previously [1, 2].

Results and Discussion

Acid Hydrolysis

In Fig. 1 the observed rate constants k^{I}_{obs}, k^{II}_{obs}, and k^{III}_{obs} are plotted as a function of the concentration of $HClO_4$. Although for solubility reasons the neutral complex $[Cr(SA)_3]$ had to be studied in a mixture of ethanol and water instead of pure water, the important finding is that the observed pH dependence (2) for both k^{I}_{obs} and k^{II}_{obs} is the same as found for k^{III}_{obs} [2]:

$$k_{obs} = k' + k''[H^+] \tag{2}$$

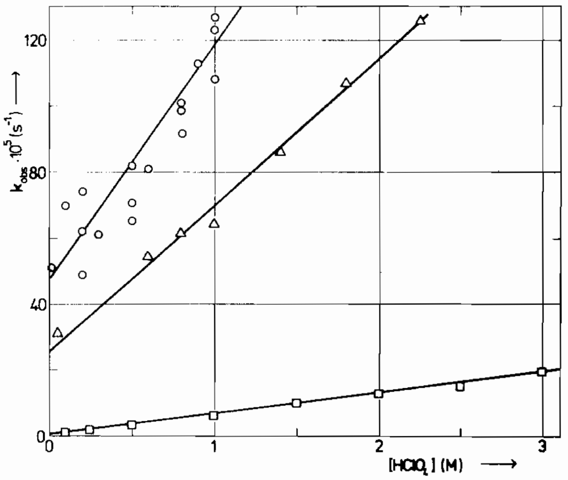


Fig. 1. Rate constants k_{obs} as a function of acid concentration. –○–○–: k^{I}_{obs} at 43 °C and ionic strength I = 1($NaClO_4$) for ethanol/water (1:1) as solvent. –△–△–: k^{II}_{obs} at 68 °C and I = 3($NaClO_4$). –□–□–: k^{III}_{obs} at 80 °C and I = 3($NaClO_4$).

This implies an acid independent (k′) and an acid dependent pathway (k″[H^+]) for all 3 steps of reaction (1).

TABLE I. Rate Constants and Activation Energy for the Acid Hydrolysis of the Species $[Cr(SA)_2]^+$ (= *II*) and $[Cr(SA)_3]$ (= *I*).

Reaction Studied	T(°C)	$k_{obs} \times 10^{-5}$ (s^{-1})	$k_o \times 10^5$ (s^{-1})	$k_1K_1 \times 10^5$ (s^{-1})	E_A[a] (kJ/mol)
II → *III*	57.5	254 ± 3	135 ± 14	122 ± 9	72.9 ± 3.4
($[HClO_4]$ = 1 N; I = 3)	61.5	363 ± 5	194 ± 63	180 ± 40	
	66.5	544 ± 3	248 ± 145	337 ± 106	
	68	637 ± 23	255 ± 24	442 ± 18	
I → *II*	35	40.9 ± 2.0	–	–	46.9 ± 2.9
(in EtOH/H_2O (1:1);	40	67.8 ± 1.7	–	–	
$[HClO_4]$ = 0.5 N; I = 1)	43	72.9 ± 4.9	47.6 ± 6.1	63.8 ± 10.0	
	53	115.3 ± 4.9	–	–	

[a] From temperature dependence of k_{obs}.

The sequence of reactions (3)–(5) with n ranging from 0 to 2 (hydration of charged species omitted) is compatible with (2) and

$$[Cr(SA)_{3-n}]^{n+} \xrightarrow{k_0} [Cr(SA)_{2-n}]^{(n+1)+} + SAH \quad (3)$$

$$[Cr(SA)_{3-n}]^{n+} + H^+ \underset{}{\overset{K_1}{\rightleftharpoons}} [Cr(SAH)(SA)_{2-n}]^{(n+1)+} \quad (4)$$

$$[Cr(SAH)(SA)_{2-n}]^{(n+1)+} \xrightarrow{k_1} [Cr(SA)_{2-n}]^{(n+1)+} + SAH \quad (5)$$

yields (6) (assumption: $K_1[H^+] \ll 1$).

$$k_{obs} = k_0 + k_1 \cdot K_1[H^+] \quad (6)$$

It is assumed that equilibrium (4) is fast and that the proton adds to one of the lone electron pairs of the phenolic oxygen, thus weakening the Cr–O bond. The rate determining process in step (5) could be the rupture of this protonated Cr–O bond, followed by fast loss of the chelate ligand.

In Table I the kinetic parameters for the hydrolysis of the species *I* and *II* are summarized.

Anion Catalysis

The acid hydrolysis of the species $[Cr(SA)]^{2+}$ has been found to be strongly catalysed by the oxo anions $HSO_4^-(SO_4^{2-})$ and NO_3^-, whereas the catalytic effect of the halide anions Cl^- and Br^- is very small [12].

Figure 2 proves that for the step $[Cr(SA)_2]^+ \rightarrow [Cr(SA)]^{2+}$ the same pattern of behaviour is observed and that there are no anion effects for the hydrolysis of the neutral complex $[Cr(SA)_3]$, *i.e.*, for step *I* → *II*.

In the experiments with added sodium sulfate, the observed catalysis of step *II* → *III* can be brought about either by HSO_4^- or by SO_4^{2-} anions, both species being in equilibrium according to (7) (K can be estimated to be 4.8 × 10^{-2} mol/l at 57.5 °C and I = 3($NaClO_4$) [17, 18]). It was proved previously [12] for the step *III* → *IV* that the doubly charged anion SO_4^{2-} is the reactive species. Its much higher catalytic effectiveness can be seen from Fig. 2.

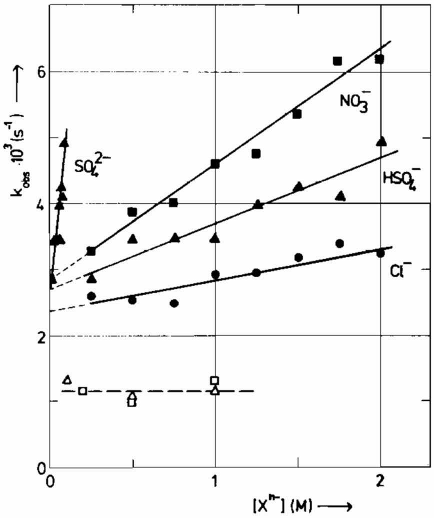


Fig. 2. Rate constants k_{obs} as a function of anion concentration. The filled symbols refer to plots of k_{obs}^{II} obtained at 57.5 °C, $[HClO_4]$ = 1 *M* and I = 3($NaClO_4$). The open symbols (□ ≙ NO_3^-, △ ≙ HSO_4^-) refer to plots of k_{obs}^{I} obtained in ethanol/water (1:1) at 51 °C, $[HClO_4]$ = 0.5 *M* and I = 1($NaClO_4$).

$$HSO_4^- \overset{K}{\rightleftharpoons} SO_4^{2-} + H^+ \quad (7)$$

As was shown for the hydrolysis of the species $[Cr(SA)]^{2+}$ by variation of the proton concentration, only the acid dependent path (k″-path in (2)) is subject to anion catalysis [12]. This would suggest a mechanistic interpretation with the protonated species $[Cr(SAH)(SA)_{2-n}]^{(n+1)+}$ (n = 0–2; see reaction (4)) interacting with the anions. The participation of oxo anions such as sulfate in the acid hydrolysis has been proved experimentally for the step *III* → *IV* in that the end product is a mixture of the cations $[Cr(H_2O)_5SO_4]^+$ and $[Cr(H_2O)_6]^{3+}$ [12].

The following scheme describes a possible interaction based on ion pair formation and subsequent coordination of the anion. The aquation of the species $[Cr(SA)_2(H_2O)_2]^+$ (= *II*; n = 1) and its protonated analogue $[Cr(SAH)(SA)(H_2O)_2]^{2+}$ is taken as an

$$[Cr(SA)_2(H_2O)_2]^+ + H^+ \overset{K_1}{\rightleftharpoons} [Cr(SAH)(SA)(H_2O)_2]^{2+} \quad (8)$$

$$[Cr(SAH)(SA)(H_2O)_2]^{2+} + X^- \overset{K_2}{\rightleftharpoons} \{[Cr(SAH)(SA)(H_2O)_2]^{2+}, X^-\} \quad (9)$$

$$\{[Cr(SAH)(SA)(H_2O)_2]^{2+}, X^-\} \xrightarrow[H_2O]{k_2} [Cr(SA)(H_2O)_3X]^+ + SAH \quad (10)$$

$$[Cr(SA)(H_2O)_3X]^+ \overset{H_2O}{\rightleftharpoons} [Cr(SA)(H_2O)_4]^{2+} + X^- \quad (11)$$

example (X^- = anion). On the basis of equations (3)–(5) and (8)–(11) one can derive (12). The parameter k^o_{obs} follows from (12) for the condition $[X^-] \rightarrow 0$. In practice, k^o_{obs}

$$k_{obs} = \frac{k_0 + k_1 \cdot K_1 [H^+] + k_2 \cdot K_1 \cdot K_2 [H^+][X^-]}{1 + K_1 [H^+] + K_1 \cdot K_2 [H^+][X^-]} \quad (12)$$

$$k^o_{obs} = \frac{k_0 + k_1 \cdot K_1 [H^+]}{1 + K_1 [H^+]} \quad (13)$$

is determined by extrapolation of the curves in Fig. 2 to $[X^-] = 0$. Remembering $K_1[H^+] \ll 1$, one can combine (12) and (13) to obtain (14). For $[H^+]$ = const. plotting of $(k_{obs} - k^o_{obs})^{-1}$ as a function of $[X^-]^{-1}$ should lead to a straight line from

$$\frac{1}{(k_{obs} - k^o_{obs})} = \frac{1}{K_1 \cdot K_2 [H^+][X^-](k_2 - k^o_{obs})} + \frac{1}{(k_2 - k^o_{obs})} \quad (14)$$

the intercept and slope of which k_2 and $K_1 \cdot K_2$ can be deduced. As can be seen from Fig. 3 for the steps *II* → *III* and *III* → *IV* and for $X^- = NO_3^-$, linear relationships are indeed obtained. For obvious reasons [1] the data for the anion catalysed hydrolysis of *II* scatter much more than those measured for *III*. The parameters k_2 and $K_1 \cdot K_2$ are compiled in

TABLE II. Kinetic Parameters for Anion Catalysed Hydrolysis of the Species $[Cr(SA)_2]^+$ (*II* → *III*) and $[Cr(SA)]^{2+}$ (*III* → *IV*) at $[HClO_4]$ = 1 *M*.

Reaction studied	$k_2 \times 10^3$ (s^{-1})			$K_1 \cdot K_2$ ($mol\ l^{-1}$)^2			K_2 (rel.)[a]			f_a[b]		
	Cl^-	NO_3^-	SO_4^{2-}	Cl^-	NO_3^-	SO_4^{2-}	Cl^-	NO_3^-	SO_4^{2-}	Cl^-	NO_3^-	SO_4^{2-}
II → *III* (I = 3; 57.5 °C)	–	3.27 ± 1.15	7.62 ± 5.10	–	0.58 ± 0.12	2.98 ± 1.87	–	0.19	1	1.03	1.53	30[c]
III → *IV* (I = 3; 70 °C)	0.16 ± 0.07	6.26 ± 1.99	7.93 ± 3.97	0.34 ± 0.14	0.18 ± 0.06	4.65 ± 2.33	0.07	0.04	1	1.8	18.7	618[c]

[a] Sulfate as reference. [b] f_a = 'acceleration factor' = k_{obs}/k^o_{obs} at $[X^-]$ = 0.5 *M*. [c] By linear extrapolation; $[SO_4^{2-}]$ calculated from $[HSO_4^-]_0$ via pk_s (HSO_4^-).

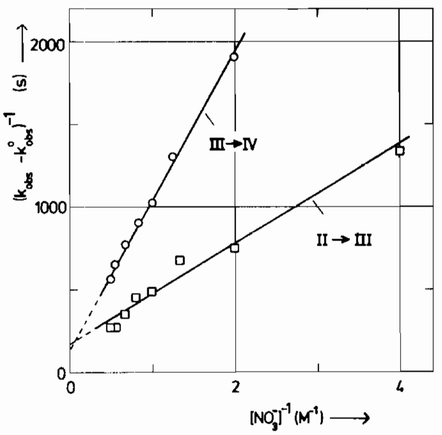


Fig. 3. The parameter $(k_{obs} - k^o_{obs})^{-1}$ as a function of nitrate concentration at $[H^+] = 1$ *M* according to equation (14). –□–□–: step *II* → *III* at 57.5 °C and for I = 3; –○–○–: step *III* → *IV* at 70 °C and for I = 3.

Table II. Although Fig. 2 reveals a very slight acceleration by chloride anions, the determination of the corresponding value for k_2 according to (14) is not possible because of too much scattering of the data.

Looking at the values of k_2 for the conversion *III* → *IV*, one is faced with the special labilizing power of the oxo anions (*cis*-effect). There is a factor of approx. 40 between $k_2(Cl^-)$ on the one hand and $k_2(NO_3^-)$ and $k_2(SO_4^{2-})$ on the other. The influence of doubly charged anions and cations on outer sphere complex formation is demonstrated by the size of $K_2(SO_4^{2-})/K_2(NO_3^-)$ and $K_2(SO_4^{2-})/K_2(Cl^-)$ for the cations *III* = $[CrSA]^{2+}$ and *II* = $[Cr(SA)_2]^+$. A comparison of the acceleration factors f_a clearly shows that the species $[CrSA]^{2+}$ with a twofold positive charge is much more subject to oxo anion catalysis than the species $[Cr(SA)_2]^+$. This is probably due to a considerable smaller value of K_2, the equilibrium constant for ion pair formation, for the latter species.The fact (see Fig. 2) that there is practically no oxo anion catalysis for the hydrolysis of the neutral species $[Cr(SA)_3]$ (= *I*) can be regarded as a further extension of this electrostatic argument. The extent of outer sphere complex formation (as described by K_2) between $[Cr(SA)_3]$ or $[Cr(SAH)(SA)_2]^+$ and oxo anions such as NO_3^- and even SO_4^{2-} seems to be very small.

A detailed comparison of the parameter $K_1 \cdot K_2$ for steps *II* → *III* and *III* → *IV* is not possible since the size of both K_1 and K_2 will change upon increasing the charge from +1 (species *II*) to +2 (species *III*).

Reaction (10) describes the incorporation of the anion X^- into the inner coordination sphere and, simultaneously, the loss of the ligand SAH. It is an open question as to what rate determining step the rate constant k_2 stands for. It could well be that the substitution of an inner sphere coordinated water molecule by the oxo anion is rate determining, *i.e.* the entrance of the oxo anion into the inner sphere from the outer sphere. The fact that within the limits of error, $k_2(NO_3^-)$ is equal to $k_2(SO_4^{2-})$ for either step *II* → *III* or step *III* → *IV*, indicates that it is the breaking of the Cr–OH₂ bond that limits the rate. In order to shed additional light on this question the anation of the cation $[Cr(H_2O)_6]^{3+}$ by sulfate anions was studied in some detail.

Anation of the $[Cr(H_2O)_6]^{3+}$ Cation by Sulfate

The formation of the species $[Cr(H_2O)_5SO_4]^+$ = *V* according to (15) was followed spectrophotometrically under the conditions of the acid hydrolysis of

$$[Cr(H_2O)_6]^{3+} + SO_4^{2-} \rightleftharpoons [Cr(H_2O)_5SO_4]^+ + H_2O \quad (15)$$

III. The rate of equilibration (as determined by Guggenheim's method [19]) increases with increasing sulfate concentration (see Table III). At low concentrations k_{obs} grows linearly but levels off at higher concentrations of sulfate.

The following sequence of reactions, as suggested by N. Fogel *et al.* [20], gives a plausible explanation (coordinated water and ion pair formation with HSO_4^- anions omitted):

$$\underset{IV}{Cr^{3+}} + SO_4^{2-} \overset{K_{IP}}{\rightleftharpoons} \underset{\text{ion pair IP}}{(Cr^{3+}, SO_4^{2-})} \quad \text{(fast)} \quad (16)$$

$$(Cr^{3+}, SO_4^{2-}) \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \underset{V}{[CrSO_4]^+} \quad \text{(slow)} \quad (17)$$

Based on reactions (16) and (17) and on the assumption of ion pair formation being fast compared to anation one can derive:

$$-\frac{d[IV]}{dt} = \alpha \cdot [IV] - \beta \cdot [IV]_0 \quad (18)$$

TABLE III. Rate of Equilibration for the Anation Reaction $Cr^{3+} + SO_4^{2-} \rightleftharpoons [CrSO_4]^+$ (T = 70 °C, $[HClO_4]$ = 1 N, I = 3($NaClO_4$)).

$[SO_4^{2-}] \times 10^2$ (*M*)	0	0.29	0.72	1.44	2.15	2.84	4.21
$k_{obs} \times 10^4$ (s^{-1})	≈0.4[a]	1.19	2.07	3.37	4.62	5.52	6.87

[a] By extrapolation.

$$\alpha = \frac{(k_3 + k_{-3})\cdot K_{IP}\cdot[SO_4^{2-}] + k_{-3}}{1 + K_{IP}[SO_4^{2-}]}$$

$$\beta = k_{-3}/(1 + K_{IP}\cdot[SO_4^{2-}])$$

$[IV]_0$ is the total concentration of chromium(III).

For the condition $[SO_4^{2-}] \gg [IV]_0$ (which was fulfilled in the experiments) integration of (18) leads to (19) and (20).

$$[IV] = [IV]_0\left[\frac{\alpha - \beta}{\alpha}\cdot e^{-\alpha\cdot t} + \frac{\beta}{\alpha}\right] \qquad (19)$$

$$[IV] - [IV]_\infty = [IV]_0\cdot\frac{\alpha - \beta}{\alpha}\cdot e^{-\alpha\cdot t} \qquad (20)$$

$[IV]_\infty$ characterizes the concentration of *IV* in reaction (15) after equilibration has occurred.

The anation of *IV* by sulfate was monitored by following the increase in absorbance A at 610 nm. It was shown experimentally that the formation of the ion pair (Cr^{3+}, SO_4^{2-}) does not change the spectrum of *IV*, which means $\epsilon(IV) \approx \epsilon$(ion pair) ($\epsilon$ = extinction coefficient). The values for k_{obs} given in Table III were obtained from the slope of the $\log(A - A_\infty)$ *versus* time plots. It can easily be shown that for $[SO_4^{2-}] \gg [IV]_0$ the parameter $(A - A_\infty)$ is directly proportional to the parameter $([IV] - [IV]_\infty)$. This relation leads to (21) as following from (20). Equation (21) reduces to

$$k_{obs} = \alpha = \frac{(k_3 + k_{-3})\cdot K_{IP}[SO_4^{2-}] + k_{-3}}{1 + K_{IP}[SO_4^{2-}]} \qquad (21)$$

$k_{obs} = k_{-3} = k^o_{obs}$ for $[SO_4^{2-}] = 0(k^o_{obs} = k_{-3} \approx 0.4 \times 10^{-4}\ s^{-1}$ can be reasonably well approximated by extrapolation in a $k_{obs} = f([SO_4^{2-}])$ diagram). Therefore, plotting of $(k_{obs} - k^o_{obs})^{-1}$ as a function of $[SO_4^{2-}]^{-1}$ should allow the determination of k_3 and K_{IP} according to (22). Figure 4 demonstrates that a linear relationship is obtained, indeed, the numbers being $k_3 = (1.65 \pm 0.11) \times 10^{-3}\ s^{-1}$ and $K_{IP} = (15.6 \pm 1)\ M^{-1}$. In comparison to the magnitude of ion pair formation constants between other complex cations of charge 3+ and sulfate anions [21] K_{IP} appears to be rather small; however, Fogel *et al.* [20] found a value of $K_{IP} \approx 10\ M^{-1}$ (T = 71 °C, I = 2.0) which is even smaller.

$$\frac{1}{(k_{obs} - k^o_{obs})} = \frac{1}{k_3\cdot K_{IP}[SO_4^{2-}]} + \frac{1}{k_3} \qquad (22)$$

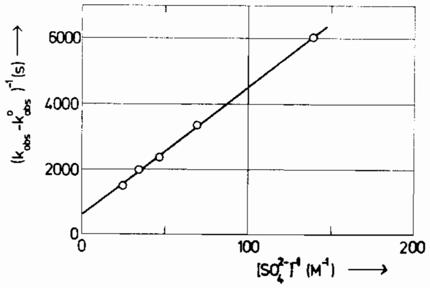
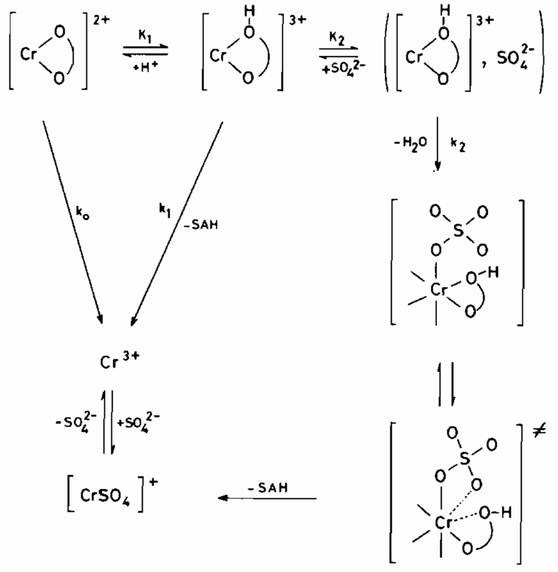


Fig. 4. The parameter $(k_{obs} - k^o_{obs})^{-1}$ as a function of reciprocal sulfate concentration for the anation of *IV* (T = 70 °C; $[HClO_4]$ = 1.0; I = 3).

Comparison of Hydrolysis and Anation

The investigation of the anation of *IV* by sulfate was undertaken to clarify the nature of the k_2-step (see reaction (10)). If the displacement of an inner sphere coordinated water molecule by an outer sphere coordinated sulfate anion is rate determining for both the sulfate catalysed hydrolysis of the species $[Cr(SA)]^{2+}$ and the anation of Cr^{3+} by SO_4^{2-}, then k_2 (reaction (10)) and k_3 (reaction (17)) ought to be of comparable size. The data obtained (70 °C; $[HClO_4]$ = 1.0; I = 3), namely $k_2 = (7.9 \pm 4.0) \times 10^{-3}\ s^{-1}$ and $k_3 = (1.7 \pm 0.1) \times 10^{-3}\ s^{-1}$ are satisfactorily close together. One can conclude, therefore, that the interpretation of the displacement of coordinated water by sulfate being rate determining in the sulfate catalysed hydrolysis of *III* is reasonable. The following scheme describes the single steps of the hydrolysis of *III* (OO–H = salicylaldehyde = SAH; hydration omitted).



This scheme assumes an associative attack of the coordinated potentially bidentate oxo anion on a *cis*-position, in agreement with suggestions made by others [5, 6]. This attack leads to a transition state with coordination number 7 (I_a-mechanism) and labilizes the bond between chromium and the protonated oxygen of the chelate ligand, thus facilitating its replacement by water. It is reasonable to assume that the oxo anion catalysis observed for step *II* → *III* occurs analogously. The question of what mechanistically is the nature of the acid independent k_0-path of hydrolysis remains unsettled.

The assignment of water for anion substitution to k_2 in the present study is not necessarily valid for other types of chromium(III) chelate complexes. It is conceivable that the rupture of the second chelate bond is rate determining, especially in those cases where the monodentate form of the chelate ligand forms stable compounds, such as $[Cr(enH)(H_2O)_5]^{4+}$ [22] and $[Cr(malH)(H_2O)_5]^{2+}$ (mal = malonate) [23].

Acknowledgments

Stimulating discussions with Dr. K. J. Wannowius are gratefully acknowledged. The authors thank the Deutsche Forschungsgemeinschaft and the Verband der Chemischen Industrie e.V. for support.

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