Rates of Chelate Ring Closure and Opening at a Chromium(III)–Thiol Bond

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Summary The rates of chelate ring opening, $(70[H^+] + 0{\cdot}6) \times 10^{-6}[Cr(H_2O)_4(SCH_2CO_2)^+]$, and closure, $(70 + 0{\cdot}8[H^+]^{-1}) \times 10^{-7}[Cr(H_2O)_5(O_2CCH_2SH)^{2+}]$, at the Cr–S bond appear to parallel other substitutions at Cr^{III} with no apparent abnormalities associated with the mercaptan function and a 100-fold rate advantage for chelate closure by both paths.

DIRECT rate measurements of either chelate ring closure at a transition-metal centre or substitution involving thiol donor groups are rare.[1] In a rapid reaction between $(en)_2Co(SCH_2CO_2)^+$ and Cr^{II}, mercaptoacetate is transferred to the Cr^{III} product.[2] The initial Cr^{III} product, believed to be $Cr(H_2O)_5(SCH_2CO_2H)^{2+}$, undergoes successive reactions to produce two new ions which were characterized by their electronic absorption spectrum and their elution characteristics from a Dowex 50W-X2 cation exchange column calibrated with comparable complexes of known charge.

The first of these secondary products elutes as a +1 ion which, together with its absorption characteristics [λ_{max} 548 (ϵ 68·3), 437 (53·4), and 264 (5070) nm], supports its formulation as the chelate, $Cr(H_2O)_4(SCH_2CO_2)^+$. After elution this ion equilibrates with a third species which can be separated out as a +2 ion with spectral characteristics [λ_{max} 568 (ϵ 26·0) and 411 (25·1) nm] expected for $Cr(H_2O)_5(O_2CCH_2SH)^{2+}$. At low acid concentrations this complex reverts back to the +1 ion.

The interconversion together with the spectrophotometrically determined rate law at constant acidity can be described by equations (1)—(3). K_1 was determined to be

$$Cr(H_2O)_4(SCH_2CO_2)^+ + H_3O^+ \underset{k_r}{\overset{k_f}{\rightleftharpoons}} Cr(H_2O)_5(O_2CCH_2SH)^{2+},\ K_1 \qquad (1)$$

$$d[Cr(H_2O)_4(SCH_2CO_2)^+]/dt = -k_f[Cr(H_2O)_4(SCH_2CO_2)^+] + k_r[Cr(H_2O)_5(O_2CCH_2SH)^{2+}] \qquad (2)$$

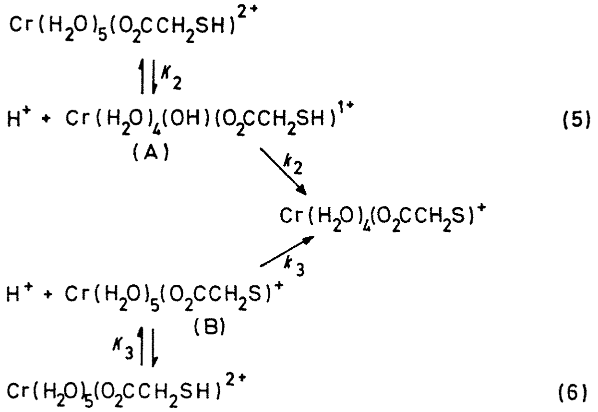
$$k_{obs} = k_f + k_r \qquad (3)$$

10·3 by chromium analyses of the two fractions eluted from an exchange column charged with equilibrium mixtures. k_f and k_r were evaluated from $k_{obs.}$ at various acidities (0·010—0·20M), 25 °C and μ = 0·25 ($LiClO_4$–$HClO_4$), by the standard procedure[3] yielding equation (4).

$$k_f = (70[H^+] + 0{\cdot}6) \times 10^{-6},\ k_r = (70 + 0{\cdot}8[H^+]^{-1}) \times 10^{-7} \qquad (4)$$

The first microscopically reversible path is interpreted as involving a net loss or gain of co-ordinated mercaptide through a transition state in which sulphur is protonated. Accordingly, mercaptoacetate enjoys a 30—250 fold rate advantage for chelate closure by RSH over that recorded for monodentate ligation of $Cr(H_2O)_6^{3+}$ by HF or HN_3.[4] A 'proton ambiguity[4]' exists for interpretation of the second path in that two intermediates can possibly participate in ring closure [see equation (5) and (6)]. From extensible data for $Cr(H_2O)_5(O_2CMe)^{2+}$,[5] we approximate K_2 as 3×10^{-5}, ignoring the question of acidity and labilizing capacity for *cis vs. trans* positions since this estimate should provide a close upper limit for the most reactive form of (A). In view of a value of $K = 6 \times 10^{-11}$ for deprotonation of mercaptoacetate,[6] K_3 seems unlikely to be greater than 10^{-8}. Combination of these estimates with the experimental rate constant yields the estimates: $k_2 = 3 \times 10^{-3}$ s^{-1}; $k_3 > 9$ s^{-1}.

We prefer mechanism (5) for ring closure by the inverse acid path in agreement with related previous analyses.[4] A particular point in its favour is that it preserves the previously noted rate advantage of approximately 10^2 for chelate closure compared to monodentate ligation of $Cr(H_2O)_5(OH)^{2+}$ by HF and HN_3.[4] While k_2 exceeds the rate of water exchange for $Cr(H_2O)_5^{3+}$,[7] a largely dissociative process does not seem unreasonable for substitution *via* k_2 in view of the expected labilization by co-ordinated hydroxide.[4] In contrast, the estimate for k_3 would require an unprecedented degree of assistance from the incoming group. While we cannot exclude this possibility rigorously it seems less likely. If a primarily dissociative mechanism is operative and our estimate of K_2 is accurate, the capacity for a pendant chelate function to "trap" a vacated co-ordination position suggests that our estimate of k_2 is a rough lower limit for water dissociation at positions *cis* to the carboxylate in (A).



Finally, mercaptide dissociation by the acid-independent path is comparable in rate to that observed for the aquation of $Cr(H_2O)_5Cl^{2+}$ ($2{\cdot}7 \times 10^{-7}$ s^{-1}).[4a] In view of this and the greater expected basicity of co-ordinated mercaptide over co-ordinated fluoride, there is no basis for believing that the rate of acid-catalysed loss is not consistent with that for the acid-catalysed aquation of $Cr(H_2O)_5F^{2+}$ ($1{\cdot}36 \times 10^{-8}$ [H^+]).[4a] Thus, our observations appear attributable to an expected rate advantage for chelate closure[1] rather than to any unusual effects associated with substitution involving thiol groups, at least when the mechanism is primarily dissociative in character.

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