Unusual Effect of Nitrous Acid on the Rate of Aquation of Acidopenta-aquochromium(III) Ions

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THE five-co-ordinate intermediate, $Cr(H_2O)_5^{3+}$, was postulated to be formed during the aquation of the iodopenta-aquochromium(III) ion.[1] An alternative explanation of Ardon's results was suggested in view of the demonstrated labilising ability of the iodo-ligand in this complex.[2] We have attempted to generate $Cr(H_2O)_5^{3+}$ by oxidising the azidopenta-aquochromium(III) ion with nitrous acid, and to trap it by means of added anions (X^-)[3] by a similar procedure to that used for $Co(NH_3)_5^{3+}$. During the course of this work we suspected that nitrous acid was catalysing the rate of aquation of expected products of the type $Cr(H_2O)_5X^{2+}$. Although nitrous, acetic, and boric acids are known to catalyse substitution reactions of square-planar platinum(II) complexes,[4] there is no evidence for such catalysis in octahedral systems. Therefore, we have investigated reactions of type (1) ($X^- = Cl^-$ or Br^-) in the presence of catalytic amounts of added acids. For comparison, we also investigated the effect of nitrous acid on the rate of aquation of the bromopenta-amminechromium(III) ion. The results are shown in the Table, together with rate constants for the hydrolysis of these complexes in the absence of catalysts.

$$Cr(H_2O)_5X^{2+} + H_2O \rightleftarrows Cr(H_2O)_6^{3+} + X^- \qquad (1)$$

Effect of additives on the rate of aquation of chromium(III) *complexes.* (μ 1·0, $NaClO_4$)

Complex	Additive	$[H^+]$[a] M	Temp. (°C)	10^4k sec.$^{-1}$
$Cr(H_2O)_5Br^{2+}$		0·10	45·0	3·1[b]
0·02M-$Cr(H_2O)_5Br^{2+}$	0·01M-HNO_2	0·10	45·0	20·5[c]
0·02M-$Cr(H_2O)_5Br^{2+}$	0·03M-HNO_2	0·10	45·0	58·0[c]
0·02M-$Cr(H_2O_5Br^{2+}$	0·01M-H_3BO_3	0·10	45·0	3·2[c]
0·03M-$Cr(H_2O)_5Br^{2+}$	0·01M-$CH_3{\cdot}CO_2H$	0·10	45·0	3·4[c]
$Cr(H_2O)_5Cl^{2+}$		0·032	50·0	0·51[d]
0·02M-$Cr(H_2O)_5Cl^{2+}$	0·01M-HNO_2	0·032	50·0	5·5[c]
$Cr(NH_3)_5Br^{2+}$		0·45	25·0	8·5[e]
0·002M-$Cr(NH_3)_5Br^{2+}$	0·05M-HNO_2	0·45	25·3	9·2[c]

[a] Free acid concentration. [b] Ref. 5 [c] This work. [d] Ref. 6. [c] Ref. 7.

The reactions were studied by spectroscopy in the range 400—700 mμ. Good isosbestic points were observed throughout the course of each reaction, the initial and final spectra agreeing with those published for the reactant complexes and the expected products, respectively. There was no spectral evidence for the formation of intermediates during the course of the reactions.

It is obvious from the results that reactions of type (1) ($X^- = Cl^-$ or Br^-) are specifically catalysed by nitrous acid, and not by small concentrations of acetic or boric acids. In this respect the catalysis reported here differs from that reported for substitution reactions of platinum(II).[4] Since nitrous acid did not significantly affect the rate of aquation of the bromopenta-amminechromium(III) ion (the *ca.* 1% observed rate enhancement can be attributed to ion-pairing effects[8]), we conclude that the catalysis must involve attack on the co-ordinated water molecules. The following mechanism appears consistent with our observations:

$$Cr(H_2O)_5X^{2+} + HNO_2 \rightleftharpoons Cr(H_2O)_4(ONO)X^+ + H_3O^+ \qquad (2)$$

$$Cr(H_2O)_4(ONO)X^+ + H_2O \rightleftharpoons Cr(H_2O)_5ONO^{2+} + X^- \qquad (3)$$

$$Cr(H_2O)_5ONO^{2+} + H_3O^+ \rightleftharpoons Cr(H_2O)_6^{3+} + HNO_2 \qquad (4)$$

Reactions (2)–(4) are expected to be rapid compared with the rate of the uncatalysed aquation reaction. Equilibria (2) and (4) are analogous to the rapid formation[9] and hydrolysis[10] reactions reported for the nitritopenta-amminechromium(III) ion. These reactions are rapid because they do not involve metal–ligand bond cleavage. Reaction (3) is also expected to be more rapid than reaction (1), *i.e.* the uncatalysed aquation, because of the different charges of the reactant complexes. A similar behaviour was suggested previously.[2] The intermediates proposed in reactions (2) and (3) have not been reported elsewhere, although the nitritopenta-aquochromium(III) ion was suggested to be formed during the inner-sphere reduction of the nitropenta-amminecobalt(III) ion with chromium(II).[11] We have prepared a compound which we believe to be the nitritopenta-aquochromium(III) ion by the reaction of an excess of nitrous acid with the hexa-aquochromium(III) ion, followed by ion-exchange separation at 0° and pH 3—4 (Cr : NO_2^-, 1·0 : 1; λ_{max} 563 mμ, ϵ_M 18·1M^{-1} cm.$^{-1}$). Since nitro-complexes of chromium(III) are unknown[12] there can be little doubt that this is the oxygen-bonded isomer. The compound undergoes a rapid acid-catalysed aquation expected for nitrito- but not nitro-complexes.[10] For example, at 10·0°, μ 1·0 ($NaClO_4$) and in the presence of a large excess of acid, the pseudo-first-order rate constant, k_0 varies with the acid concentration as: $[H^+] = 0{\cdot}10$M, $10^2k_0 = 4{\cdot}7$ sec.$^{-1}$; $[H^+] = 0{\cdot}99$M, $10^2k_0 = 158$ sec.$^{-1}$ The rate of formation of the complex was also observed to be relatively rapid. These results confirm the rapid nature of equilibria (2) and (4), and establish the likelihood that nitrito-intermediates are involved in the nitrous acid catalysis of reactions of type (1).

Since it is necessary to study reactions of type (1) in acidic media to reduce the formation of conjugate bases of the type[5,6] $Cr(H_2O)_4(OH)X^+$, under such conditions equilibrium (2) must lie well to the left, and equilibrium (4) well to the right. This explains the lack of spectral evidence for the formation of the postulated intermediates.

We are investigating the kinetics of these reactions further to establish the detailed nature of the mechanisms.

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