Kinetics of Aquation and Formation of the Tetra-aqua(2,2′-bipyridyl)-chromium(III) Ion †

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Kinetics of aquation of the tetra-aqua(2,2′-bipyridyl)chromium(III) ion and of its formation from bipy and hexa-aquachromium(III) ion has been studied as a function of acidity and Cr^{3+} concentration at 1·0M ionic strength ($NaClO_4$). No build-up of the unidentate bipy intermediate has been observed and with an excess of Cr^{3+} ion present the first-order rate constant for the approach to equilibrium is given by $k_{obs.} = k_1[Cr^{3+}] + (k_{-1}k_{-2}/k_2)$. At 140·2 °C the second-order formation rate constant $k_1 = (2{\cdot}0 \pm 0{\cdot}1) \times 10^{-3}[H^+]^{-1} + (7{\cdot}0 \pm 1{\cdot}4) \times 10^{-6} [H^+]^{-2}$ l mol^{-1} s^{-1} and the composite term $k_{-1}k_{-2}/k_2 = (9{\cdot}5 \pm 0{\cdot}2) \times 10^{-5} + (6{\cdot}3 \pm 0{\cdot}3) \times 10^{-7}[H^+]^{-1}$ s^{-1}. Speculative breakdown of the composite term yields the rate of ring closure $k_2 = 5{\cdot}3$ s^{-1} and the rate of bond rupture $k_{-1}' = 1{\cdot}3 \times 10^{-2}$ s^{-1} for the intermediate $[Cr(OH_2)_5(bipy)]^{3+}$ ion, giving $k_2/k_{-1}' = 408$.

2,2′-BIPYRIDYL (bipy) continues to be frequently used as a suitable ligand for kinetic studies of substitution reactions of transition-metal complexes.[1-7] A preliminary investigation of the Cr^{3+}–bipy system in nitrate media led to the isolation of diaquabis(2,2′-bipyridyl)chromium(III) trinitrate.[8] After detailed kinetic study of the aquation of penta-aquapyridinechromium(III) [9] and *cis*-tetra-aquabis(pyridine)chromium(III) ions,[10] it seemed proper to prepare and to investigate the kinetic behaviour of the mono(2,2′-bipyridyl) complex of chromium(III). While this work was in progress preparation of the complex ion by another route was reported.[11]

The preparation of monosubstituted chromium(III) complexes with unidentate aliphatic polyamines [12-15] prompted the question as to whether the analogous unidentate bipy complex could exist as a relatively stable species in solution, in spite of the low conjugated acid-dissociation constant for the second nitrogen atom of the free ligand. A negative conclusion on this point can be drawn from the work presented here, in which we report a kinetic study of the aquation of tetra-aqua(2,2′-bipyridyl)chromium(III) ion and of its formation from bipy and hexa-aquachromium(III) ion as a function of acidity and excess of Cr^{3+}.

EXPERIMENTAL

Preparation of Tetra-aqua(2,2′-bipyridyl)chromium(III) *Ion.*—The (2,2′-bipyridyl)oxodiperoxochromium(VI) species [16] is readily formed as a blue precipitate by addition of 2 mol equivalents of H_2O_2 to an equivalent mixture of chromate ion and bipy dissolved in a minimal amount of water. A suspension of the blue species in 1M-$HClO_4$ decomposed on heating back to chromate ion, probably by dissociation of peroxo-ligands and by their subsequent decomposition.‡ However, agitation of the suspension in 1M-$HClO_4$ for *ca.* 20 h at 40 °C with a constantly present excess of H_2O_2 led to a red solution containing mainly $[Cr(OH_2)_4(bipy)]^{3+}$ ion. The complex ion was separated from small amounts of chromium(III) ions formed and higher-charged polymeric species using a Dowex 50W-X8 ion-exchange column, from which it was eluted with 3M-$HClO_4$. The concentration of $[Cr(OH_2)_4(bipy)]^{3+}$ in solutions obtained in this way was of the order of 5×10^{-3}M. The acidity of some stock solutions was reduced at 0 °C to 10^{-2}M by dropwise addition to 3M-NaOH for use in kinetic studies at lower acidities. While this work was in progress a different and less convenient preparative procedure was reported.[11]

Other Materials.—Potassium dichromate or chromium(VI) oxide, 2,2′-bipyridyl, 30% hydrogen peroxide, 70% perchloric acid, and sodium hydroxide, all Merck analytical grade, were used without further purification. All solutions were prepared with doubly distilled water.

Analytical Methods.—Chromium(III) was determined spectrophotometrically as chromate ion (ε $4{\cdot}815 \times 10^3$ l mol^{-1} cm^{-1} at 375 nm) after decomposition of the complex and oxidation with alkaline peroxide.[17] Interference from bipy absorption was negligible; bipy present in the complex ion was also determined spectrophotometrically at 296 nm (ε $1{\cdot}38 \times 10^4$ l mol^{-1} cm^{-1}), after aquation of the complex at 150 °C in 1·0M-$HClO_4$. The concentration of perchloric acid in solutions of the complex was determined by the method of King and Neptune.[18] All absorption measurements for analytical and kinetic purposes were made on Beckman DU-2, Hilger H-700, and Unicam SP 700 spectrophotometers.

Kinetic Measurements.—In kinetic runs ampoules containing aliquot portions of the reaction mixtures were kept at 140·2 ± 0·2 °C in a thermostat filled with suitable paraffinic

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† Presented at the 3rd Yugoslav Congress of Pure and Applied Chemistry, Ljubljana, 1972. Taken from the thesis submitted by R. Marčec in partial fulfilment of the requirements for the M.Sc. degree at the University of Zagreb, 1972.

‡ 1M = 1 mol dm^{-3}.

[1] D. J. Benton and P. Moore, *J.C.S. Dalton*, 1973, 399; *J.C.S. Chem. Comm.*, 1972, 717.

[2] P. K. Chattopadhyay and J. F. Coetzee, *Inorg. Chem.*, 1973, **12**, 113.

[3] J. C. Cassat, W. A. Johnson, L. M. Smith, and R. G. Wilkins, *J. Amer. Chem. Soc.*, 1972, **94**, 8399.

[4] J. Burgess, *J.C.S. Dalton*, 1972, 1061.

[5] W. S. Melvin, D. P. Rablen, and G. Gordon, *Inorg. Chem.*, 1972, **11**, 488.

[6] J. P. Rund, *Inorg. Chem.*, 1972, **11**, 499.

[7] G. B. Briscoe, M. E. Fernandopulle, and W. R. McWhinnie, *Inorg. Chim. Acta*, 1972, **6**, 598.

[8] R. G. Inskeep and J. Bjerrum, *Acta Chem. Scand.*, 1961, **15**, 62.

[9] A. Bakač and M. Orhanović, *Inorg. Chem.*, 1971, **10**, 2443.

[10] A. Bakač, M.Sc. Thesis, University of Zagreb, 1972.

[11] S. Y. Ng, and C. S. Garner, *Inorg. Chim. Acta*, 1971, **10**, 2443.

[12] R. F. Childers, jun., K. G. Vander Zyl, jun., D. A. House, R. G. Hughes, and C. S. Garner, *Inorg. Chem.*, 1968, **7**, 749.

[13] D. K. Lin and C. S. Garner, *J. Amer. Chem. Soc.*, 1969, **91**, 6673.

[14] R. L. Wilder, D. A. Kamp, and C. S. Garner, *Inorg. Chem.*, 1971, **10**, 1393.

[15] S. J. Ranney and C. S. Garner, *Inorg. Chem.*, 1971, **10**, 2437.

[16] J. E. Fergusson, C. J. Wilkins, and J. F. Young, *J. Chem. Soc.*, 1962, 2136.

[17] G. W. Haupt, *J. Res. Nat. Bur. Stand.*, 1955, **48**, 2331.

[18] E. L. King and J. A. Neptune, *J. Amer. Chem. Soc.*, 1955, **77**, 3186.

oil. At known times ampoules were immersed in a cooled diethyl ether bath to stop the reaction and to remove the oil. The progress of the reaction was analysed spectrophotometrically by following an inverse change in the optical density at 330 and 280 nm. At these wavelengths ε values ($\mathrm{l\ mol^{-1}\ cm^{-1}}$) for $[\mathrm{Cr(OH_2)_4(bipy)}]^{3+}$ ion are $5{\cdot}1 \times 10^3$ and $2{\cdot}8 \times 10^3$; those of bipy in 1M-$\mathrm{HClO_4}$ are $2{\cdot}8 \times 10^2$ and $9{\cdot}2 \times 10^3$, while the values in 6×10^{-3}M-$\mathrm{HClO_4}$ (I = 1·0M) are $3{\cdot}8 \times 10^2$ and $6{\cdot}7 \times 10^3$. The rate constants were calculated from gradients of straight lines obtained for three or more half-lives of the reaction by plotting $\log(D_e - D_t)$ or $(D_t - D_e)$ against time, where D_t and D_e are the optical densities at time t and 10 half-lives of the reaction, respectively. Similar results were obtained at both wavelengths. The amount of the complex ion (as % of the total bipy) present at equilibrium after 8—10 half-lives of the reaction was calculated from the expression $[\mathrm{Cr(bipy)^{3+}}] = 100\ (D_\infty - D_e)/(D_\infty - D_0)\%$ for data in Table 1 or from $[\mathrm{Cr(bipy)^{3+}}] = 100\ (D_e - D_0)/(D_\infty - D_0)\%$ for data in Table 2, where D_0 is the optical density of the reaction mixture before the start of the reaction and D_∞ the calculated optical density expected for the complete aquation (Table 1) or the complete formation reaction (Table 2).

TABLE 1

First-order rate constants for the approach to equilibrium in the aquation of $[\mathrm{Cr(OH_2)_4(bipy)}]^{3+}$ at 140·2 °C and 1M ionic strength ($\mathrm{HClO_4 + NaClO_4}$)

$[\mathrm{H^+}]$/ mM	$10^2[\mathrm{Cr(bipy)^{3+}}]$/ mM	$10[\mathrm{Cr^{3+}}]$ added/ mM	10^4k_{obs}/ $\mathrm{s^{-1}}$	$[\mathrm{Cr(bipy)^{3+}}]$ at equilibrium/%
800	12·4	0	0·98	4·9
800	12·4	30·5	1·03	9·9
800	12·4	100	1·22	20·3
800	12·4	200	1·44	30·9
100	12·7	0	1·00	7·5
100	12·7	6·35	1·16	16·9
100	12·7	19·0	1·39	31·3
100	12·7	31·7	1·63	41·8
100	12·7	45·0	1·94	49·3
100	12·7	62·0	2·26	57·3
100	12·7	100	2·93	67·8
100	12·7	240	6·08	82·6
30·6	6·02	0	1·11	8·8
15·0	6·02	0	1·41	10·8
10·0	2·41	0	1·60	11·2
10·0	2·41	2·50	2·41	39·7
10·0	2·41	4·88	3·35	53·6
10·0	2·41	10·1	4·72	67·8
10·0	2·41	20·3	7·23	76·5
10·0	12·4	23·7	7·80	75·8
7·50	6·02	0	1·75	16·7
6·00	6·00	0	2·01	15·5

TABLE 2

First-order rate constants for the approach to equilibrium in the formation of $[\mathrm{Cr(OH_2)_4(bipy)}]^{3+}$ at 140·2 °C and 1M ionic strength ($\mathrm{HClO_4 + NaClO_4}$)

$[\mathrm{H^+}]$/ mM	$10^2[\mathrm{bipy}]$/ mM	$10[\mathrm{Cr^{3+}}]$/ mM	10^4k_{obs}/ $\mathrm{s^{-1}}$	$[\mathrm{Cr(bipy)^{3+}}]$ at equilibrium/%
100	12·7	19·0	1·42	29·1
100	12·7	31·7	1·74	39·3
100	12·7	45·0	1·78	46·0
100	12·7	62·0	2·16	56·2
100	12·7	100	3·00	69·6
100	12·7	170	4·45	76·3
100	12·7	240	5·50	81·1
30·6	6·05	18·3	2·54	51·2
30·6	6·05	36·0	4·27	64·2
15·0	6·05	12·2	3·40	57·7
15·0	6·05	18·3	4·27	69·7
10·0	2·41	2·50	1·89	33·9
10·0	2·41	4·88	3·35	50·2
10·0	2·41	10·1	4·67	60·3
7·50	6·02	4·40	3·55	50·8
7·50	6·02	8·14	4·81	63·1
7·50	6·02	12·2	5·92	69·2
6·00	6·00	6·10	5·25	62·5
6·00	6·00	11·9	8·25	69·7

In the runs involving aquation, reaction concentrations of the complex ion varied in the range $(1{\cdot}27—0{\cdot}241) \times 10^{-4}$M, while in runs involving the formation reaction concentrations of bipy varied in the range $(1{\cdot}26—0{\cdot}240) \times 10^{-4}$M. Spectra of the ' infinite time ' samples in the preliminary work were not satisfactorily reproducible, probably due to oxidative impurities attacking (the relatively low concentration of) bipy at the high reaction temperature. Addition of isopropyl alcohol (to make it 10^{-2}M in the reaction mixture) removed this difficulty, and did not interfere with kinetic or stoicheiometric measurements.

RESULTS

Spectra of Tetra-aqua(2,2′-bipyridyl)chromium(III) *Ion*.—The visible and near u.v. spectra of tetra-aqua(2,2′-bipyridyl)chromium(III) ion were the same in 0·1—3M-aqueous perchloric acid and in 0·1—1M-$\mathrm{HClO_4}$ at 1M ionic strength ($\mathrm{NaClO_4}$), showing absorption ($\varepsilon/\mathrm{l\ mol^{-1}\ cm^{-1}}$) at 529 (max.) (27·2), 465 (min.) (10·7), 442(sh) (31·2), 413(sh) (85·3), 389 (max.) (132), and 387 nm (min.) (130). Our value for the absorption intensity of the first *d–d* transition band deviates slightly from the one reported by Ng and Garner [11] for a 4M-$\mathrm{HNO_3}$ medium (528 nm, ε 29·5 $\mathrm{l\ mol^{-1}\ cm^{-1}}$) and it is also similar to the value for *cis*-tetra-aquabis(pyridine)chromium(III) ion in perchlorate media (533 nm, ε 25·9 $\mathrm{l\ mol^{-1}\ cm^{-1}}$).[10] The u.v. spectrum (Figure 1) was unaffected by change of acidity in the range $1{\cdot}9 \times 10^{-2}$—1·0M at 1·0M ionic strength and by 3M-$\mathrm{HClO_4}$. The spectral data refer to 25 °C.

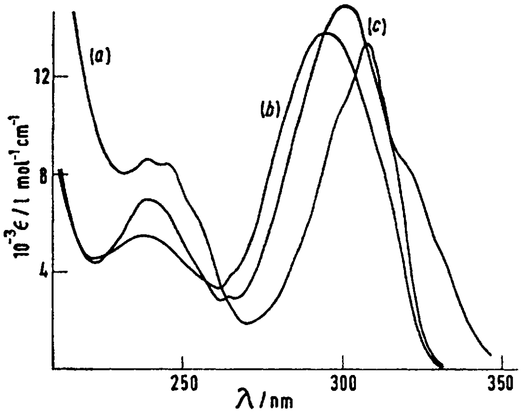
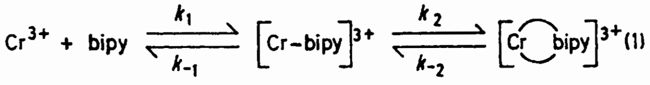


FIGURE 1 U.v. absorption spectra of: (*a*) $[\mathrm{Cr(OH_2)_4(bipy)}]^{3+}$ in 1·0M-$\mathrm{HClO_4}$; (*b*), bipy in 1·0M-$\mathrm{HClO_4}$; and (*c*), bipy in 0·006M-$\mathrm{HClO_4}$ at I = 1·0M ($\mathrm{NaClO_4}$)

Preliminary Kinetic Experiments and Stoicheiometry.—Preliminary kinetic runs with $1{\cdot}27 \times 10^{-4}$M-complex in 1M-$\mathrm{HClO_4}$ showed that aquation of $[\mathrm{Cr(OH_2)_4(bipy)}]^{3+}$ was a very slow first-order process, with the specific rate $2{\cdot}8 \times 10^{-4}\ \mathrm{s^{-1}}$ at 151 °C. The u.v. spectrum changed gradually to that of completely dissociated bipy with isosbestic points at 304 and 263 nm, in good agreement with isosbestic points shown in Figure 1 for a 1M-$\mathrm{HClO_4}$ medium. U.v. absorption spectra of free and chromium(III)-bound bipy differ significantly and the hypothetical reaction intermediate involving unidentate bipy, $[Cr(OH_2)_5(bipy)]^{3+}$, would be expected to have another distinct u.v. spectrum. The clear isosbestic points observed during the aquation indicate that the unidentate bipy intermediate is likely to be present in low concentration.

The same conclusion is reached on kinetic grounds. The rate of aquation of this intermediate is expected to be similar to those of penta-aquapyridinechromium(III) ion, which would have a rate constant of $2\cdot3 \times 10^{-2}$ s^{-1} at 151 °C in 1M-$HClO_4$,[9] a factor of 80 faster than aquation of the bidentate bipy complex. The rate of chelate ring opening in the latter is expected to be of the same order of magnitude as the aquation rate of the first pyridine from *cis*-$[Cr(OH_2)_4(py)_2]^{3+}$, which would aquate with $k = 3\cdot4 \times 10^{-1}$ s^{-1} at 151 °C in 1M-$HClO_4$.[10] The inertness of the bipy complex thus appears to be mainly controlled by a high rate of rechelation and the standard reaction scheme [19] is applicable to the



$$Cr^{3+} + bipy \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Cr{-}bipy]^{3+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Cr\,bipy]^{3+} \quad (1)$$

chromium(III)–bipy reaction with the k_1 path missing in the case of complete dissociation of the complex.

Addition of Cr^{3+} ions to the reaction mixture led to an equilibrium, the same extent of which was reached for the same experimental conditions by either aquation of the complex or by its formation from Cr^{3+} and bipy, as routinely observed from the u.v. spectra in the 250—350 nm region. The isosbestic points were well preserved at all acidities and Cr^{3+} concentrations studied, and appeared at 263—264 and 306—309 nm depending on the acidity used, in agreement with the spectra in Figure 1.

Kinetics of Aquation and Formation of $[Cr(OH_2)_4(bipy)]^{3+}$ *Ion*.—First-order rate constants obtained at different concentrations of Cr^{3+} and different acidities are given in Tables 1 and 2. The amount of $[Cr(OH_2)_4(bipy)]^{3+}$ present at equilibrium after 10 half-lives of the reaction is given in the fifth column of the Tables. A high concentration of added Cr^{3+} ions was used to ensure that the formation component of the observed process was pseudo-first order. In experiments involving the aquation process and no Cr^{3+} ions added (some data in Table 1), $k_{obs.}$ was calculated from the first half-life of the reaction to avoid interference from the formation reaction. The ionic strength was kept constant with sodium perchlorate.

Assuming the stationary state for the relatively highly reactive unidentate bipy complex, the rate constant observed is given by equation (2). On the basis of the

$$k_{obs.} = \frac{k_{-1}k_{-2}}{k_{-1} + k_2} + \frac{k_1k_2[Cr^{3+}]}{k_{-1} + k_2} \qquad (2)$$

previous consideration that $k_2 \gg k_{-1}$, expression (2) reduces to (3). In agreement with equation (3), the rate

$$k_{obs.} = (k_{-1}k_{-2}/k_2) + k_1[Cr^{3+}] \qquad (3)$$

constants from Tables 1 and 2 were linearly dependent on $[Cr^{3+}]$, as shown in Figure 2 for some acidities. At a particular acidity, both sets of rate constants, those for aquation and formation, fell on the same line. The gradients (k_1) and intercepts ($k_{-1}k_{-2}/k_2$) of the lines, computed using a non-linear least-squares program, are given in Table 3.

The last two columns in Table 3 show good agreement between the apparent stability constants for $[Cr(OH_2)_4(bipy)]^{3+}$ obtained from kinetic and thermodynamic data. The latter values, $K_{eq} = [Cr(bipy)^{3+}]/[bipy][Cr^{3+}]$, were calculated from concentrations of the species present at equilibrium at 'infinite' reaction times using data from Tables 1 and 2. Mean values of K_{eq} for the particular acidities were calculated only for conditions with at least 15% of $[Cr(OH_2)_4(bipy)]^{3+}$ or bipy present at equilibrium.

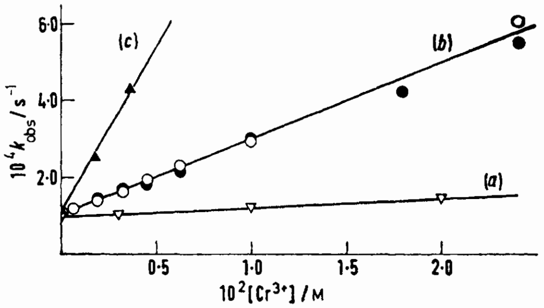


FIGURE 2 Dependence of the first-order rate constant on excess of Cr^{3+} for the approach to equilibrium in the aquation (open circles) and formation (full circles) of $[Cr(OH_2)_4(bipy)]^{3+}$ at 140·2 °C and I = 1·0M ($NaClO_4$). [$HClO_4$] = 0·8 (*a*), 0·1 (*b*), and 0·0306M (*c*)

TABLE 3

Rate constants for aquation and formation of $[Cr(OH_2)_4(bipy)]^{3+}$ ion at 140·2 °C and 1M ionic strength ($HClO_4$ + $NaClO_4$)

$[H^+]$/ mM	10^3k_1/ l mol^{-1} s^{-1}	$10^5(k_{-1}k_{-2}/k_2)$/s^{-1}	$10^{-2}(k_1k_2/k_{-1}k_{-2})$/ l mol^{-1}	$10^{-2}K_{eq}$/ l mol^{-1}
800	2·36	9·71	0·254	0·24
100	19·7	10·2	1·93	2·1
30·6	84·1	11·0	7·65	5·4
15·0	159	14·1	11·4	12
10·0	288	15·6	18·3	20
7·5	361	17·8	20·2	22
6·0	527	20·1	26·2	25

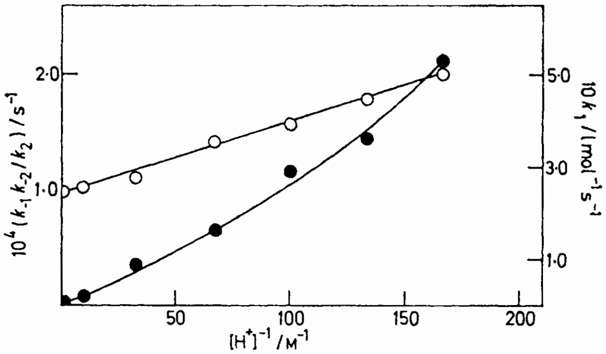


FIGURE 3 Dependence of the second-order formation rate constant k_1 (full circles) and composite term $k_{-1}k_{-2}/k_2$ (open circles) on inverse acidity for aquation and formation of $[Cr(OH_2)_4(bipy)]^{3+}$ at 140·2 °C and I = 1·0M ($NaClO_4$)

Both k_1 and $k_{-1}k_{-2}/k_2$ increased with decreasing acidity as shown in Figure 3. The least-squares treatment of the

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[19] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' John Wiley, New York, 1967, p. 223.

linear dependence of $k_{-1}k_{-2}/k_2$ on inverse acidity gives equation (4). The dependence of k_1 on the inverse acidity

$$k_{-1}k_{-2}/k_2 = (9{\cdot}48 \pm 0{\cdot}18) \times 10^{-5} + (6{\cdot}28 \pm 0{\cdot}26) \times 10^{-7}[\mathrm{H}^+]^{-1}\ \mathrm{s}^{-1} \quad (4)$$

was best fitted with the two term expression (5).

$$k_1 = (1{\cdot}97 \pm 0{\cdot}11) \times 10^{-3}[\mathrm{H}^+]^{-1} + (7{\cdot}0 \pm 1{\cdot}4) \times 10^{-6}[\mathrm{H}^+]^{-2}\ \mathrm{l\ mol^{-1}\ s^{-1}} \quad (5)$$

DISCUSSION

Linear dependence of $k_{-1}k_{-2}/k_2$ on $[\mathrm{H}^+]^{-1}$ for the reaction studied stems from protolytic equilibria involving aqua-ligands bound to $\mathrm{Cr^{III}}$ and from the k_{-1} and k_{-2} processes.[20] Protonation of the unidentate bipy ligand in the intermediate would reduce the rate of rechelation (k_2) and would tend to show up as an acid-catalysed path in the aquation kinetics; the $k_{-1}k_{-2}/k_2$ value at the highest acidity used (0·8M) deviates only 1·6% from the fitted straight line, indicating that no H^+-catalysed path operates in the acidity range studied and that the k_2 process is acid independent. This behaviour is consistent with an expected low $\mathrm{p}K_\mathrm{a}$ value for the unidentate bipy. Thus protonation of the first nitrogen atom in the free ligand leads to $\mathrm{p}K_\mathrm{a}$ −0·52 for the second nitrogen,[21] and 3+ charge on $\mathrm{Cr^{III}}$ probably decreases this value even more. Among the bivalent metal ions, lack of acid catalysis was recently found for dissociation of bipy from $\mathrm{Mn^{II}}$ in methanol,[1] in contrast to the direct observation of catalysis for $\mathrm{Ni^{II}}$ and $\mathrm{Fe^{II}}$ [22] and an indirect observation for $\mathrm{Cu^{II}}$ in aqueous media.[23,24]

In an attempt to break down the term $k_{-1}k_{-2}/k_2$, a fair estimation of k_{-1} is possible. A linear correlation was recently found between the logarithm of the rate constant and $\mathrm{p}K_\mathrm{a}$ of the free ligand for the aquation of a series of $[\mathrm{Cr(OH_2)_5(Xpy)}]^{3+}$ ions (Xpy = substituted pyridine).[25] Linearity retained on extrapolation of the rate data to 140·2 °C. It is reasonable to assume that the aquation of the unidentate bipy intermediate fits the linear correlation and the aquation rate constants $k_{-1}' = 1{\cdot}30 \times 10^{-2}\ \mathrm{s^{-1}}$ for the acid-independent path and $k_{-1}'' = 4{\cdot}7 \times 10^{-3}\ \mathrm{l\ mol^{-1}\ s^{-1}}$ for the acid-inverse path can be extrapolated at $\mathrm{p}K_\mathrm{a}$ 4·35, the $\mathrm{p}K_\mathrm{a}$ of bipy.[26] The preceding consideration implies that the acid-independent term in expression (4) corresponds to the reaction of $[\mathrm{Cr(OH_2)_4(bipy)}]^{3+}$ and $[\mathrm{Cr(OH_2)_5(bipy)}]^{3+}$ species, while the acid-inverse term is a composite term itself involving aqua- and monohydroxo-forms of the two species. Substitution of k_{-1}' in the first term of (4) gives $k_{-2}'/k_2 = 7{\cdot}3 \times 10^{-3}$, or the stability constant $K_2 = k_2/k_{-2} = 137$ for the $[\mathrm{Cr(OH_2)_4(bipy)}]^{3+}$ species.

An estimation of k_{-2}' is less certain. It was found that the rate of ring opening (k_{-2}) in monobipyridyl and monoethylenediamine complexes of $\mathrm{Ni^{II}}$, and speculatively for $\mathrm{Pt^{II}}$, is an order of magnitude slower than the rate of bond rupture in the respective unidentate intermediates (k_{-1}).[27-29] An energy barrier related to rotation of the freed end of the bidentate ligand was invoked to account for the rate difference. With chromium(III) the situation appears different; $[\mathrm{Cr(OH_2)_5X}]^{n+}$ (X = $\mathrm{Hen^+}$, $\mathrm{H_2dien^{2+}}$, $\mathrm{H_3trien^{3+}}$, and $\mathrm{H_4tetren^{4+}}$) and $[\mathrm{Cr(OH_2)_4Y}]^{n+}$ (Y = en, $\mathrm{Hdien^+}$, $\mathrm{H_2trien^{2+}}$, and $\mathrm{H_3tetren^{3+}}$) * were isolated as stable species in solution.[12-15] The directly measured aquation rates of bi- and uni-dentate complexes gave $k_{-2}/k_{-1} = 2{\cdot}7$ at 60 °C for en with a further increase to 8 and 15 for sterically more crowded dien and trien complexes. Similar behaviour is to be expected for bipy and it seems that the k_{-2}' value for $[\mathrm{Cr(OH_2)_4(bipy)}]^{3+}$ is best approximated by the aquation rate of *cis*-$[\mathrm{Cr(OH_2)_4(py)_2}]^{3+}$, which aquates a factor of 9·5 faster than $[\mathrm{Cr(OH_2)_5(py)}]^{3+}$ at 90 °C. Extrapolated to 140·2 °C, the aquation rate constant for the *cis*-bis(pyridine) species *via* the acid-independent path has the value $3{\cdot}9 \times 10^{-2}\ \mathrm{s^{-1}}$.[10] Substitution of the value of k_{-2}' so obtained in the acid-independent value of $k_{-1}k_{-2}/k_2$ from expression (4) leads to $k_2 = 5{\cdot}3\ \mathrm{s^{-1}}$ for $[\mathrm{Cr(OH_2)_5(bipy)}]^{3+}$ ion. The estimated value of $k_2/(k_2 + k_{-1}')$, 0·998 at 140·2 °C and I = 1·0M, shows that bond rupture in $[\mathrm{Cr(OH_2)_5(bipy)}]^{3+}$ species occurs 0·2% and ring closure 99·8% of the time.

The second-order formation rate constant k_1 is consistent with $k_1 = K_f k_f$, where K_f is the cation–dipole association equilibrium constant and k_f the first-order rate constant for the first bond formation. $[\mathrm{H}^+]^{-1}$ and $[\mathrm{H}^+]^{-2}$ Paths for the formation reaction presumably arise from involvement of $\mathrm{Cr^{3+}}$, $[\mathrm{Cr(OH)}]^{2+}$, bipy, and $\mathrm{Hbipy^+}$ species.

[3/1533 *Received, 23rd July*, 1973]

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* en = Ethylenediamine, dien = 3-azapentane-1,5-diamine, trien = 3·6-diazaoctane-1,8-diamine, and tetren = 3,6,9-triazaundecane-1,11-diamine.

[20] M. Orhanović and M. Avdagić, *Inorg. Chem.*, 1973, **12**, 492.

[21] F. M. Westheimer and O. T. Benfey, *J. Amer. Chem. Soc.*, 1956, **78**, 3509.

[22] F. Basolo, J. C. Hayes, and H. M. Neumann, *J. Amer. Chem. Soc.*, 1953, **75**, 5102; 1954, **76**, 3807.

[23] T. S. Roche and R. G. Wilkins, *Chem. Comm.*, 1970, 1681.

[24] H. Diebler, *Ber. Bunsengesellschaft Phys. Chem.*, 1970, **74**, 268.

[25] A. Bakač, R. Marčec, and M. Orhanović, *Inorg. Chem.*, 1974, **13**, 57.

[26] R. Näsänen, *Suomen Kem.*, 1955, **28**, 61.

[27] A. K. S. Ahmed and R. G. Wilkins, *J. Chem. Soc.*, 1959, 3700.

[28] D. W. Margerum, D. B. Rorabacher, and J. F. G. Clarke, jun., *Inorg. Chem.*, 1963, **2**, 667.

[29] M. J. Carter and J. K. Beattie, *Inorg. Chem.*, 1970, **9**, 1233.