Formation and Kinetics of Decomposition of Monoaquobis(ethylenediamine)(pyridylmethyl)chromium(III) Complexes

By **C. T. Loo, Lai-Yoong Goh,** and **S. H. Goh,*** Department of Chemistry, University of Malaya, Kuala Lumpur, Malaysia

Monoaquobis(ethylenediamine)(pyridylmethyl)chromium(III) complexes, $2\text{-}NC_5H_4CH_2Cr(en)_2(H_2O)^{2+}$ and $3\text{-}NC_5H_4CH_2Cr(en)_2(H_2O)^{2+}$, are prepared by the reduction of the corresponding picolyl chlorides by the $Cr^{II}(en)_2{}^{2+}$ ion. The decomposition of these ions is studied in 0·01—1·0M-perchloric acid and in acetate buffers of pH 1—7. Spectral changes show that these complexes undergo aquation before carbon–chromium bond cleavage. Product studies as well as kinetic data and activation parameters obtained indicate that the 2- and 3-ions decompose *via* the penta-aquo-derivative, $2\text{-}NC_5H_4CH_2Cr(H_2O)_5{}^{2+}$, and the trisaquo-derivative, $3\text{-}NC_5H_4CH_2Cr(en)(H_2O)_3{}^{2+}$ respectively. Acetate-ion catalysis is also observed for the decomposition of these ions.

THE reaction of chromium(II) ions with organic halides has received increasing attention recently. Earlier studies have indicated that chromous ions reduce organic halides with great avidity and in some instances stable organo-chromium(III) complexes result. Anet[1] obtained an air-stable red solution of penta-aquodichloromethylchromium(III) ions while Johnson[2-4] had isolated several pyridylmethylchromium(III) complexes in solution. Unstable and air-stable alkyl and aralkyl chromium(III) complexes have also been studied by Kochi.[5] More recently, Taube[6] reported the formation and aquation of penta-aquochromium(III) ions of the type $(H_2O)_5CrL^{2+}$ where L is derived from ethyl alcohol, propyl alcohol, or diethyl ether by hydrogen abstraction with OH radicals. While an increasing number of penta-aquo(alkyl)chromium(III) ions have been studied, little is known of the nature of similar complexes when the aquo-ligands are replaced by other ligands. Recently, Kochi reported the reduction of alkyl halides with chromium(II)–ethylenediamine complexes but only very unstable alkylethylenediaminechromium(III) complexes were found.[7,8] This paper reports the preparation of air-stable 2- and 3-pyridylmethyl(ethylenediamine)-chromium(III) complexes and a kinetic study of their decomposition.

EXPERIMENTAL

Perchloric acid was B.D.H. analytical grade, sodium perchlorate was Merck reagent grade and sodium acetate was Hopkin and Williams hydrated analytical grade. 2- and 3-Picolyl chloride hydrochloride were obtained from Raschig and Aldrich, respectively.

Visible and u.v. absorption spectra were recorded on a Beckman DB-G instrument, the cell compartment of which was thermostatted to ±0·2° for kinetic measurements.

Preparation of Ethylenediamine–Chromium(III) *Complexes.*—*Monoaquobis*(*ethylenediamine*)(3-*pyridylmethyl*)*chromium*-(III) *Perchlorate* (1b). Degassed ethylenediamine (18 g, 300 mmol) was added to a 0·74M-solution of chromous perchlorate (135 ml, 100 mmol) under nitrogen. A purple solution resulted with evolution of heat and some purple solids were precipitated. Immediate injection of an aqueous solution (15 ml) of 3-picolyl chloride hydrochloride (8·2 g, 50 mmol) gave a deep red solution out of which some purplish red solids were precipitated. This was stirred for 20 min at 25° and then filtered. The deep purple solids, which were filtered off (*ca.* 5 g), had no absorption in the u.v. region and were probably inorganic solids. The deep red filtrate, showing $\lambda_{max.}$ 290 and 264 nm with shoulders at 271 and 505 nm, was added to acetone–ether (*ca.* 2 l) and a deep red oil was precipitated. The oil was dissolved in a minimum amount of aqueous methanol. Addition of successive lots of methanol–ether removed most of the inorganic by-products as purple solids (7·3 g) which had $\lambda_{max.}$ 385 and 510 nm in 2M-HCl with extinction coefficients conforming to those reported for *cis*-$Cr(en)_2(H_2O)Cl^{2+}$.[9] The final lots of purplish red solids (total 4·5 g) showed $\lambda_{max.}$ 292 nm (intense) and $\lambda_{min.}$ 256—261 nm. The chromium content was analysed by conversion into $CrO_4{}^{2-}$.[10] The organic content was obtained by decomposition of the compound in acid in the presence of air to 3-picoline.[11] The solids were found to contain a ratio of 3·7 chromium atoms to 1 pyridyl group, *i.e.* it was 27·4% pure on a molar basis and the yield was 2·5 mmol (5·2%). Based on this estimated purity, the extinction coefficients of the absorption bands are as given in Table 1.

Monoaquobis(*ethylenediamine*)(2-*pyridylmethyl*)*chromium*-(III) *Perchlorate* (1a).—This compound was prepared in the same way as the 3-isomer. Analysis of Cr and organic content of the isolated solids indicated a molar ratio of 2·5 Cr to 1 pyridyl group, *i.e.* a molar purity of 40% and yield 3 mmol or 6%. Based on this estimated purity the spectral characteristics are as given in Table 1.

An attempt was made to separate the monoaquobis-(ethylenediamine)(2-pyridylmethyl)chromium(III) ions from the inorganic complex ions by cation-exchange chromatography on an IR-120(H) Amberlite Resin at 0 °C. Unfortunately, the u.v. spectra of the eluates in 5M-$HClO_4$ indicated that the complex ions had undergone aquation to

---

[1] F. A. L. Anet and E. Leblanc, *Canad. J. Chem.*, 1959, **37**, 58.

[2] R. G. Coombes, M. D. Johnson, and N. Winterton, *J. Chem. Soc.*, 1965, 7029.

[3] R. G. Coombes and M. D. Johnson, *J. Chem. Soc.* (*A*), 1966, 177, 1805.

[4] R. G. Coombes, M. D. Johnson, M. L. Tobe, N. Winterton, and Lai-Yoong Wong, *Chem. Comm.*, 1965, 251.

[5] J. K. Kochi and D. D. Davis, *J. Amer. Chem. Soc.*, 1964, **86**, 5264.

[6] W. Schmidt, J. H. Swinehart, and H. Taube, *J. Amer. Chem. Soc.*, 1971, **93**, 1117.

[7] J. K. Kochi and P. E. Mocadlo, *J. Amer. Chem. Soc.*, 1966, **88**, 4094.

[8] J. K. Kochi and J. W. Powers, *J. Amer. Chem. Soc.*, 1970, **92**, 137.

[9] D. J. MacDonald and C. S. Garner, *J. Amer. Chem. Soc.*, 1961, **83**, 4152.

[10] G. W. Haupt, *J. Res. Nat. Bur. Stand.*, 1952, **48**, 414.

[11] H. C. Brown and X. R. Mihm, *J. Amer. Chem. Soc.*, 1955, **77**, 1723.

the penta-aquo(2-pyridylmethyl)chromium(III) ions. It may be noted that the pure penta-aquo(2-pyridylmethyl)-chromium(III) ions may be separated in this manner.[2]

The solid perchlorate salts, probably a mixture of *cis*- and *trans*-isomers, were air-stable and remained unchanged for months at 0°.

Kinetic Measurements.—The kinetic runs were carried out on (1—3) × 10^{-4}M solutions of the complex ions in perchloric acid solution with the ionic strength maintained at 1·0M with sodium perchlorate, and in buffers of pH 1—7 made from 1M-HClO$_4$ and 1M-sodium acetate. Measurements of pH were made using a Pye model-78 pH meter.

TABLE 1

Absorption spectra of pyridylmethylchromium(III) ions

Complex ion	Solvent	$\lambda_{max.}$ (nm)	($\varepsilon \times 10^{-3}$) (l mol^{-1} cm^{-1})	$\lambda_{min.}$ (nm)	($\varepsilon \times 10^{-3}$) (l mol^{-1} cm^{-1})
3-pyCH$_2$Cr(en)$_2$(H$_2$O)$^{2+}$	H$_2$O (pH 6·4)	292—293	(7·9)	258	(5·5)
	0·1M-HClO$_4$	290—291	(7·5)	251	(5·3)
		515	(0·23)	455	(0·17)
2-pyCH$_2$Cr(en)$_2$(H$_2$O)$^{2+}$	H$_2$O	265·5	(4·5)	251	(4·0)
		331	(4·8)	295	(2·3)
		520	(0·22)	452	(0·14)
	0·2M-HClO$_4$	264—265	(4·9)	247—249	(4·0)
		329—330	(5·0)	291—292	(2·2)
3-pyCH$_2$Cr(H$_2$O)$_5{}^{2+}$ [a]	pH 1	285	(15)		
		320	(9·6)		
		534	(0·049)		
	Acetate buffer, pH 5	289			
		325			
2-pyCH$_2$Cr(H$_2$O)$_5{}^{2+}$ [a]	pH 1	262	(6·2)		
		318	(10·4)		
		550	(0·073)		
	Acetate buffer, pH 5	266			
		333			

[a] Data from ref. 3.

The kinetics of decomposition was followed spectrophotometrically at or close to the absorbance maxima of the complex ions. It was found that as in the case of the penta-aquo-complexes,[3,12] complicated kinetics were obtained in the presence of a limited amount of air. Hence to ensure that the reaction proceeded in the presence of an excess of air, the solution was shaken up at frequent intervals in the thermostat. Rate coefficients were calculated by standard methods for first-order reactions from the change in absorbance with time.

TABLE 2

First-order rate coefficients for the decomposition of monoaquobis(ethylenediamine)(3-pyridylmethyl)chromium-(III) ion in perchloric acid

[Complex] = 1·5 × 10^{-4}M, μ = 1M

Temp. (°C)	[HClO$_4$]/M	10^5k/s^{-1}
50·2	0·01	9·8
50·2	0·1	10·0 [a]
50·2	1·0	9·8
35·4	1·0	1·23
45·2	1·0	4·90
55·0	1·0	22·2 [b,c]
64·0	1·0	83

[a] For 3-pyCH$_2$Cr(H$_2$O)$_5{}^{2+}$, k = 19·4 × 10^{-5} s^{-1}. [b] In the presence of 6 molar excess of Cr(en)$_2$(H$_2$O)Cl^{2+}, k = 20·0 × 10^{-5} s^{-1}. [c] For the penta-aquo(3-pyridylmethyl)chromium(III) ion, Johnson [3] reported a first-order rate coefficient of 43·3 × 10^{-5} s^{-1}.

The rate constants are given in Tables 2—5. Kinetic runs carried out in the presence of varying amounts of a large excess of the isolated inorganic by-products mainly *cis*-Cr(en)$_2$(H$_2$O)Cl^{2+} ion, also gave similar rates for both the 3-ion and the 2-ion. A kinetic run in 1M-HClO$_4$ at 75·2° was also carried out using the 2-pyCH$_2$(en)$_2$(H$_2$O)$^{2+}$ ion prepared *in situ* and a similar rate coefficient was obtained (Table 3). For convenience, all other kinetic runs were performed using the isolated solid complexes.

Product Studies.—In order to isolate the products, decomposition had to be performed using 0·05—0·1M solutions. The organic products were extracted by ether–methylene chloride mixture from the reaction mixture after basification and were estimated by u.v. and ^{1}H n.m.r. spectroscopy or g.l.c. on a 2 ft SE-30 column. The following results were obtained for the 2-ion (1a): (*a*) in 1M-H$_2$SO$_4$ under nitrogen, 2-pyCH$_3$ (11%) and (2-pyCH$_2$–)$_2$ (50%); (*b*) in 1M-H$_2$SO$_4$ under oxygen, 2-pyCH$_3$ (13%) and 2-pyCO$_2$H (54%); (*c*) in pH 6 buffer under nitrogen, 2-pyCH$_3$ (40%) and (2) pyCH$_2$–)$_2$ (33%) and (*d*) in pH 6 buffer under oxygen,

TABLE 3

First-order rate coefficients for the decomposition of monoaquobis(ethylenediamine)(2-pyridylmethyl)chromium-(III) ion in perchloric acid

[Complex] = 2 × 10^{-4}M, μ = 1M

Temp. (°C)	Reaction medium	10^5k/s^{-1}
55·0	1M-HClO$_4$	1·60 [a]
75·2	1M-HClO$_4$	43·3
75·2	1M-HClO$_4$	42·8 [b]
75·2	1M-HClO$_4$	42·7 [a,c]
75·2	0·1M-HClO$_4$	38·9
65·0	0·1M-HClO$_4$	7·42
55·0	0·1M-HClO$_4$	1·15

[a] Corresponds to the spectral change $\lambda_{max.}$ 318 nm to $\lambda_{max.}$ 262·5 nm. Two faster stages preceding this can be detected. These correspond to spectral changes of λ_{max} 330 nm to $\lambda_{max.}$ 327 nm and $\lambda_{max.}$ 327 nm to $\lambda_{max.}$ 318 nm and had rate constants of *ca.* 6 × 10^{-4} s^{-1} and *ca.* 1 × 10^{-4} s^{-1}, respectively, at 25·0°. [b] In the presence of 10 molar excess of Cr(en)$_2$(H$_2$O)Cl^{2+} ions. [c] For 2-pyCH$_2$Cr(en)$_2$(H$_2$O)$^{2+}$ ion prepared *in situ*.

---

[12] A. R. Schmidt and T. W. Swaddle, *J. Chem. Soc.* (*A*), 1970, 1927.

Table 4

First-order rate coefficients for the decomposition of monoaquobis(ethylenediamine)(3-pyridylmethyl)chromium(III) ion in acetate buffers

[Complex] = (1—2) × 10^{-4}M, μ = 1M

Temp. (°C)	pH	$10^5k/s^{-1}$
25·2	1·0	4·45
25·2	2·0	7·95
34·8	2·0	23·0
45·0	2·0	74·8
25·2	3·0	11·8 [a]
25·2	4·0	16·7
25·2	5·0	24·7 [b]
25·2	5·6	13·8 [c]
25·2	6·0	24·6 [d,e]
34·8	6·0	70·6
44·8	6·0	200
25·2	7·0	25·1

[a] For 3-$\mathrm{pyCH_2Cr(H_2O)_5^{2+}}$, $k = 18{\cdot}1 \times 10^{-5}\ \mathrm{s^{-1}}$. [b] [Acetate] = 0·77M. [c] [Acetate] = 0·09M. [d] In the presence of 10 molar excess of $\mathrm{Cr(en)_2(H_2O)Cl^{2+}}$, $k = 24{\cdot}0 \times 10^{-5}\ \mathrm{s^{-1}}$. [e] For 3-$\mathrm{pyCH_2Cr(H_2O)_5^{2+}}$, $k = 70{\cdot}2 \times 10^{-5}\ \mathrm{s^{-1}}$.

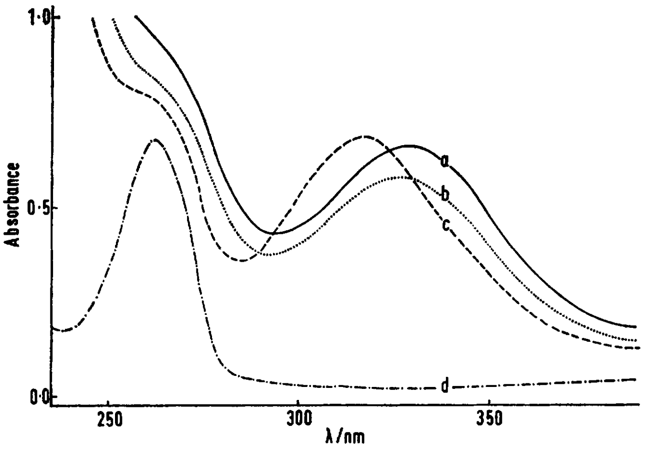
Table 5

First-order rate coefficients for the decomposition of monoaquobis(ethylenediamine)(2-pyridylmethyl)chromium(III) ion in acetate buffers

[Complex] = (1·5—2·5) × 10^{-4}M, μ = 1M

Temp. (°C)	pH	$10^4k/s^{-1}$
40·0	1·0	0·0872
40·0	2·2	0·253
40·0	3·1	0·776
40·0	4·1	1·99
40·0	5·0	2·32
40·0	5·4	2·46
40·0	6·0	2·26

mainly 2-$\mathrm{pyCO_2H}$ and some 2-$\mathrm{pyCH_2OH}$. For the 3-ion the following results were obtained: (*a*) in 1M-$\mathrm{HClO_4}$ under nitrogen, 3-$\mathrm{pyCH_3}$ (20%) and (3-$\mathrm{pyCH_2}$–$)_2$ (40%); (*b*) in 1M-$\mathrm{HClO_4}$ under oxygen, 3-$\mathrm{pyCH_3}$ (30%), 3-pyCHO (10%), 3-$\mathrm{pyCO_2H}$ (30%), and 3-$\mathrm{pyCH_2OH}$ (*ca.* 10%); (*c*) in pH 6 buffer under nitrogen, 3-$\mathrm{pyCH_3}$ (4%) and (3-$\mathrm{pyCH_2})_2$ (30%), and (*d*) in pH 6 buffer under oxygen, 3-$\mathrm{pyCH_3}$ (28%) and 3-$\mathrm{pyCO_2H}$ (50%). Free ethylenediamine was detected in all cases.



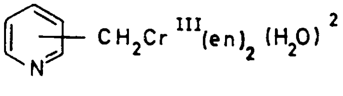
Changes in the u.v. absorption spectrum of $2\overset{+}{\mathrm{H}}\mathrm{pyCH_2Cr(en)_2(H_2O)^{2+}}$ (*ca.* 1·3 × 10^{-4}M) in 1M-perchloric acid: a, initial spectrum; b, after 30 min at 25·0°; c, after 20 h at 25°; d, after 6 days at 55·0°

RESULTS AND DISCUSSION

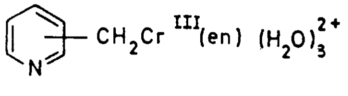
Preparation and Properties of Monoaquobis(ethylenediamine)(pyridylmethyl)chromium(III) *Complexes.*—Treatment of 2- and 3-picolyl chloride with an aqueous solution of $\mathrm{Cr^{II}(en)_2}^{2+}$ made from ethylenediamine and chromous ions in a molar ratio of 3 : 1,[13] gave the corresponding complex ions (1a) and (1b), according to the following equations: [8]

$$\mathrm{pyCH_2Cl + Cr(en)_2^{2+} \longrightarrow pyCH_2\cdot + ClCr(en)_2^{2+}} \qquad (1)$$

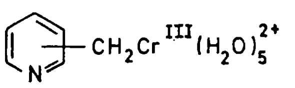
$$\mathrm{pyCH_2\cdot + Cr(en)_2^{2+} \longrightarrow pyCH_2Cr(en)_2^{2+}} \qquad (2)$$



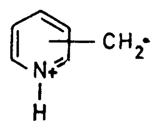
(1a) 2-picolyl complex
(1b) 3-picolyl complex



(2a) 2-picolyl complex
(2b) 3-picolyl complex



(3a) 2-picolyl complex
(3b) 3-picolyl complex



(4)

The spectral changes of 2-$\mathrm{pyCH_2Cr(en)_2(H_2O)^{2+}}$, (1a), in 1M-perchloric acid with time are shown in the Figure. The initial absorption showed $\lambda_{\mathrm{max.}}$ 330 nm which after about 30 min at 25° changed to $\lambda_{\mathrm{max.}}$ 327 nm, the absorption assigned to the mono-ethylenediamine complex ion (2a), which was subsequently converted into the relatively stable penta-aquo(2-pyridylmethyl)chromium(III) ion (3a), $\lambda_{\mathrm{max.}}$ 318 nm after *ca.* 20 h. Finally, at a higher temperature, the penta-aquo ion (3a) decomposed *via* carbon–chromium bond cleavage. The spectral characteristics of the bis(ethylenediamine) complex ions given in Table 1 show similar features to those previously reported by Johnson [2] for the corresponding penta-aquo-ions.

The 3-$\mathrm{pyCH_2Cr(en)_2(H_2O)^{2+}}$ ion (1b) is less stable than the 2-ion (1a). In 1M-perchloric acid solution at 35 °C the absorption maximum 290 nm shifted to 285 nm in *ca.* 15 min, the intensity of the latter band subsequently decreased following a first-order rate law. The initial absorption band at 290 nm was assigned to (1b) and the 285 nm band to the 3-$\mathrm{pyCH_2Cr(en)(H_2O)_3^{2+}}$ ion (2b). Kinetic data discussed below indicate that (2b) decomposed directly *via* carbon–chromium bond cleavage

---

[13] R. L. Pecsok and J. Bjerrum, *Acta Chem. Scand.*, 1957, **11**, II, 1418.

rather than through the penta-aquo-derivative (3b) formed by further aquation.

Product and Kinetic Studies.—The final products of the decomposition of the complex ions (1a) and (1b) were Cr^{3+} ions and several pyridyl compounds. In the absence of oxygen the major organic products that could be isolated by extraction with organic solvents were ethylenediamine, picoline, and dipyridylethane. In the presence of oxygen or air, pyridinecarboxaldehyde and pyridinecarboxylic acid were the main products in addition to some picoline. The formation of picoline and dipyridylethane in the absence of oxygen or pyridinecarboxaldehyde and acid in the presence of oxygen may be expected on the basis of the formation of the radical (4). These findings are in agreement with the results of Johnson.[3] The similarity of products for the presently reported complexes containing ethylenediamine ligands makes it likely that the same mode of decomposition is operative, *i.e.* carbon–chromium bond homolysis rather than heterolysis. This homolytic mechanism appears to be unique for these pyridylmethyl chromium complexes [3] though for related benzyl chromium complexes Kochi [14] has reported evidence for heterolytic cleavage. It has been reported [3] that the radical (4) is not particularly sensitive to oxygen as picoline can form even in its presence. Alternatively, however, picoline may arise from the same radical (4) by electron transfer from chromium(II) ions by the mechanism suggested by Schmidt and Swaddle,[12] or by hydrogen abstraction from co-ordinated water molecules as proposed by Johnson [3] and by Schmidt and Swaddle.[12] Pyridylmethanol was also isolated from the reactions carried out in the presence of air. This may be explained as arising from the oxidation of the radical (4) to give peroxidic intermediates, the subsequent decomposition of which by metal ions [15] can lead to the observed carbinol.

The decomposition of the organochromium ions was studied in perchloric acid as well as in acetate buffer. In perchloric acid, three distinct stages were observed for the 2-ion (1a) and two for the 3-ion (1b). The initial faster stages were not followed. Good first-order kinetics were obtained for the final slower stage to more than 90% of the reaction. The kinetic data are given in Tables 2 and 3. The kinetic results in perchloric acid at constant ionic strength show no dependence on acid concentration (Table 2). Various amounts of added inorganic impurity, mainly *cis*-$Cr(en)_2(H_2O)Cl^{2+}$, in 5—10 fold excess, did not significantly affect the rates. Moreover, in the case of the 2-ion (1a), the rate of decomposition in 1M-$HClO_4$ of the isolated solid is the same as that of the complex ion prepared *in situ*.

The spectral changes corresponding to the three observed stages of the decomposition of the 2-ion in 1M-$HClO_4$ are illustrated in the Figure. The kinetic results from these spectral changes coupled with the detection of free ethylenediamine in the products may be explained by the relatively rapid aquation of the ion before carbon–chromium bond cleavage. The first stage probably corresponds to the replacement of one ethylenediamine molecule, equation (3), and the second to the loss of a second ethylenediamine molecule, equation (4). More complicated schemes for stepwise displacement of ethylenediamine [16-19] may be envisaged but the present data is insufficient for this distinction to be made. In

$$\overset{+}{H}pyCH_2Cr(en)_2(H_2O)^{2+} + 2H_2O \longrightarrow \overset{+}{H}pyCH_2Cr(en)(H_2O)_3{}^{2+} + en \tag{3}$$

$$\overset{+}{H}pyCH_2Cr(en)(H_2O)_3{}^{2+} + 2H_2O \longrightarrow \overset{+}{H}pyCH_2Cr(H_2O)_5{}^{2+} + en \tag{4}$$

$$\overset{+}{H}pyCH_2Cr(H_2O)_5{}^{2+} \longrightarrow \overset{+}{H}pyCH_2\cdot + Cr(H_2O)_5{}^{2+} \tag{5}$$

the third stage, equation (5), the decrease in the absorption band $\lambda_{max.}$ 317—318 nm (corresponding to the dissociation of the carbon–chromium bond) occurred simultaneously with the increase of u.v. absorption at *ca.* 260 nm due to the formation of organic pyridyl compounds. The kinetics of this third stage are in fact identical to those of decomposition of the penta-aquochromium ion (3a) previously studied.[3]

It was shown that the rate coefficient for the 3-ion in 1·0M-$HClO_4$ at 55° is significantly different from that of the penta-aquochromium ion (3b) previously studied.[3] The observed spectral changes and kinetics may be described by equations (3) and (6):

$$3\text{-}\overset{+}{H}pyCH_2Cr(en)(H_2O)_3{}^{2+} \longrightarrow 3\text{-}\overset{+}{H}pyCH_2\cdot + Cr(en)(H_2O)_3{}^{2+} \tag{6}$$

In acetate buffers the reaction is definitely catalysed, a finding also reported by Johnson for similar complex ions 2-$pyCH_2Cr(H_2O)_5{}^{2+}$ (3a) and 3-$pyCH_2Cr(H_2O)_5{}^{2+}$ (3b). Rate coefficients for the final stage of the reaction in different pH buffers and different temperatures are tabulated in Tables 4 and 5. It may be pointed out that the rates for the 3-ion (1b) are different from those of the decomposition of the 3-$pyCH_2Cr(H_2O)_5{}^{2+}$ ion. The variation of rates with pH means that different protonated species of the ion decompose at different rates. From the data given in Tables 4 and 5, pK_a values of 3·4 and 3·2 may be obtained for the 2-ion and 3-ion respectively; these values agree well with Johnson's value of pK_a *ca.* 3 for the analogous penta-aquochromium ions.[2]

Rates of aquation of (ethylenediamine)chromium(III) complexes are generally slow.[9,17-21] The rapid aquation

---

[14] J. K. Kochi and D. Buchanan, *J. Amer. Chem. Soc.*, 1965, **87**, 853.

[15] W. A. Waters, 'Mechanisms of Oxidation of Organic Compounds,' Wiley, New York, 1964, p. 36.

[16] H. L. Schlafer, *J. Inorg. Nuclear Chem.*, 1960, **13**, 101.

[17] H. L. Schlafer and O. Kling, *J. Inorg. Nuclear Chem.*, 1958, **8**, 320.

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

[19] A. D. Kirk, K. C. Moss, and J. G. Valentin, *Canad. J. Chem.*, 1971, **49**, 375.

[20] D. J. MacDonald and C. S. Garner, *Inorg. Chem.*, 1962, **1**, 20.

[21] J. M. Veigel and C. S. Garner, *Inorg. Chem.*, 1965, **4**, 1569.

observed here is somewhat surprising and not readily explained. However, there is a reported case *i.e.*, $\text{Cr(en)(C}_2\text{O}_4)_2^-$ (k = *ca.* 10^{-5}—10^{-4} s^{-1}, 20°)[16] with an aquation rate close to ours.

The activation parameters for the decomposition of the $2\text{-pyCH}_2\text{Cr(en)}_2(\text{H}_2\text{O})^{2+}$ and $3\text{-pyCH}_2\text{Cr(en)}_2(\text{H}_2\text{O})^{2+}$ ions in perchloric acid and acetate buffers presented in Table 6, are determined for the final stage of the decomposition, *i.e.* the cleavage of the carbon–chromium bond. In perchloric acid medium the magnitude of the enthalpies of activation ($\Delta H^{\ddagger}$ *ca.* 30 kcal mol^{-1}) is compatible with previous studies of the analogous penta-aquo-ions.[3] The values of $\Delta H^{\ddagger}$ = 37·0 kcal mol^{-1} and $\Delta S^{\ddagger}$ = +30 cal deg^{-1} mol^{-1} for the 2-ion in 0·1M-HClO_4 are exactly identical with values obtained by Johnson for the penta-aquo-ion (3a), indicating that the aquation reactions, equations (3) and (4), did occur and it was the penta-aquo-derivative that finally decomposed, equation (5). For the 3-ion, however, the activation enthalpy of 30·6 kcal mol^{-1} is different from that of the penta-aquo-ion (33·3 kcal mol^{-1}).[3] This together with the observation that only two stages are distinguishable show that the decomposition is that of the $3\text{-H}\overset{+}{\text{py}}\text{CH}_2(\text{en})(\text{H}_2\text{O})_3^{2+}$ ion (2b) rather than the completely aquated ion. This would indicate that the rate of carbon–chromium bond dissociation in (2b) is faster or comparable to the rate of displacement of an ethylenediamine molecule by water molecules. In acetate buffers, activation parameters obtained were much lower. In the case of the 3-ion, $\Delta H^{\ddagger}$ values were 20·7 and 19·1 kcal mol^{-1} at pH 2 and pH 6, respectively, with corresponding values of $\Delta S^{\ddagger}$ equal to −8 and −12 cal deg^{-1} mol^{-1}. These results as well as the enhanced kinetics are indicative of catalytic pathways. The values are also compatible with those obtained for the decomposition of other organochromium ions in the presence of acetate.[3,14]

TABLE 6

Activation parameters

Complex ion	pH	$\Delta H^{\ddagger} \pm 1$ (kcal mol^{-1})	$\Delta S^{\ddagger} \pm 1$ (cal deg^{-1} mol^{-1})
$3\text{-pyCH}_2\text{Cr(en)}_2(\text{H}_2\text{O})^{2+}$	1·0M-HClO_4	30·6	+17
	pH 6	19·1	−12
	pH 2	20·7	−8
$3\text{-pyCH}_2\text{Cr(H}_2\text{O)}_5^{2+}$ [a]	1·02M-HClO_4	33·3 ± 1	+26 ± 5
$2\text{-pyCH}_2\text{Cr(en)}_2(\text{H}_2\text{O})^{2+}$	0·1M-HClO_4	37·0	+30
$2\text{-pyCH}_2\text{Cr(H}_2\text{O)}_5^{2+}$ [a]	0·1M-HClO_4	37·2 ± 1	+30 ± 5

[a] Data from ref. 3.

The authors thank Mr. Chiam Yeow Boon for technical assistance.

[1/1479 *Received*, 17*th August*, 1971]