action with V(III). The authors correctly point out that, in the event, assignment of any resonance position as reflecting strictly pH is problematic. With regard to the in-range peak, if taken to reflect acidity, the derived pH 6.9 is a reasonable value for the cytoplasm of the vanadocyte, which could easily contribute a phosphate resonance to the whole-cell experiment. In any case, a vanadophoric pH 6.9 is clearly inconsistent with other results presented and discussed herein.

From the anaerobic lysis experiments (iii, above), Hawkins and co-workers attempted to account for the total acidity liberated as arising from a combination of the internal acidity originally present, augmented by the acid generated following lyolytic hydrolysis of trivalent vanadium and iron released from the vanadophore. However, the total acid produced (3.15×10^{-5} mol from 0.5 mL of packed cells) is so much greater than that which was estimated to be caused by metal hydrolysis (1.3×10^{-5} mol) that the remainder back-calculates to a vanadophoric concentration[24] of 0.28 M H_2SO_4. This is most likely an unrealistic figure, and indeed the authors suggested that the extra acidity may derive from the release of protons when V(III) is chelated following cell lysis. The analytical results presented here support this latter possibility since much of the liberated vanadium was found bound to cellular debris (Table I).

In any case, among Phlebobranchs, and possibly Aplousobranchs, at least one of the vanadium-accumulating tunicates appears to maintain this metal ion at a pH less than 2. Significantly, this pH is sufficient to convert absorbed oceanic orthovanadate ion completely to the monopositive VO_2^+ ion.[36] Thus these data stand in support of the acidic reduction mechanism of vanadium accumulation by tunicates proposed by Macara et al.[60]

The small concentration of vanadyl ion found within the vanadocyte seems to militate against any important functional role for this ion in *A. ceratodes*. It seems more reasonable to suppose that it represents vanadium only partially reduced from ingested vanadate and trapped as vanadyl ion when the cells were frozen. A similar hypothesis has been made for vanadyl ion in *A. nigra* following vanadate uptake studies.[3] If true, then vanadyl ion concentration within the vanadocyte would be a complex function of feeding rate and oceanic vanadate concentration. It would, therefore, be expected to fluctuate about some small value, as has been observed.

The utility of V(III) to tunicates remains an unresolved question; however, any hypothesis must explicitly take note of the low oxidation state in which this ion is maintained.[24] The contents of vanadophores are now known to comprise a surprisingly complex mixture, with 1.4 M V(III), ~1 M tunichromes, 1.3 M sulfate, ~0.85 M complex sulfur of possibly novel types, plus other metals, and possibly other constituents stored in a low-pH solution. How these materials contribute to the fitness with which tunicates respond to environmental stress is likely to be found in the functional role of the vanadophore, e.g. in the production of test, in the immune response, or as a defense against surface fouling, among others. It is, therefore, not necessary inter alia to restrict the functional significance of any particular vanadophoric constituent either to the interior of the vanadophore or to interaction with a second vanadophoric constituent. In that regard, we suggest[50] that V(III) might produce peroxide-like species following exposure to the aerobic, mildly alkaline[61,62] intertidal environment wherein these animals are found. Such reagents, if produced on site by vanadocyte lysis subsequent to minor injury,[63,64] might forestall bacterial invasion, as well as possibly seal off such injuries by sclerotization of the surrounding tissue. This suggestion is consistent with the known oxidative chemistry of, e.g., peroxovanadates,[65] as well as the wound-healing activity of vanadocytes.

Acknowledgment. We thank W. L. Campbell for performing the ICP atomic emission spectroscopic analyses, and S. P. McDonald for the X-ray fluorescence spectral analysis of the $BaSO_4$ sample. This work was supported by the National Science Foundation through Grant PCM 82-08115.

Registry No. S, 7704-34-9; V, 7440-62-2; Fe, 7439-89-6; Zn, 7440-66-6; Cr, 7440-47-3; Cu, 7440-50-8; VO^{2+}, 20644-97-7; SO_4^{2-}, 14808-79-8; Co^{2+}, 22541-53-3; V^{3+}, 22541-77-1; Cl^-, 16887-00-6; ClO_4, 14797-73-0; H_2SO_4, 7664-93-9; $VO(H_2O)_5^{2+}$, 15391-95-4; P, 7723-14-0.

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σ-Bonded Organochromium(III) Complexes. 3. Decomposition in Acid Solution of Chromium(III) Complexes Containing Pyridylmethyl and Polydentate Amine Ligands[1,2]

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Received June 11, 1985

The decomposition of σ-bonded (pyridylmethyl)chromium complexes, 2- and 3-$NC_5H_4CH_2CrL_n$ (L = dap (1,3-diaminopropane), dien (diethylenetriamine), trien (triethylenetetramine), and [15]aneN$_4$ (tetraazacyclopentadecane)), was investigated in aqueous perchloric acid under aerobic conditions. Except for L = 15[ane]N$_4$, Cr–C bond scission was preceded by complete aquation in the case of the 2-isomers and partial aquation for the 3-isomers. The aquation rates were compared with those of inorganic chromium complexes containing similar amine ligands. Kinetic data for the Cr–C bond cleavage were correlated with those for the analogous ethylenediamine (en) and aquo (H_2O) systems. The activation parameters and product studies are in support of a homolytic pathway for the Cr–C bond cleavage.

Reactions of organochromium complexes such as hydrolysis, protonolysis, oxidation, and polymerization and reactions with $HgCl_2$, $TlCl_3$, halogens, and organic halides have received considerable attention[3-5] and form the subject of a recent review.[6] In particular, the mechanistic aspects of the chromium–carbon

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(1) Part 2: Crouse, K.; Goh, L. Y. *Inorg. Chim. Acta* **1985**, *99*, 199-205.
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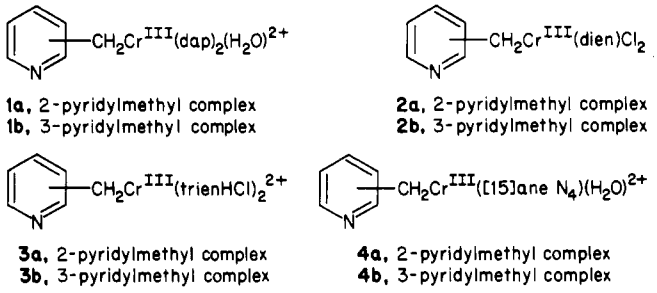
Chart I



1a, 2-pyridylmethyl complex
1b, 3-pyridylmethyl complex
2a, 2-pyridylmethyl complex
2b, 3-pyridylmethyl complex
3a, 2-pyridylmethyl complex
3b, 3-pyridylmethyl complex
4a, 2-pyridylmethyl complex
4b, 3-pyridylmethyl complex

bond cleavage in these complexes is of continuing interest.[7-9] However, most of this work has been centered around the $(H_2O)_5CrR^{2+}$ cation although in one earlier report we have described the decomposition of the 2- and 3-$NC_5H_4CH_2Cr(en)_2(H_2O)^{2+}$ ions in acid.[10] Since then, no work seems to have appeared in the literature on the mechanistic studies of Cr–C bond scission in such $(amine)_xCrR^{2+}$ systems. In a continuing investigation into the factors that may affect the mode of scission of the σ-bond in carbon–chromium complexes,[1,11] we have varied the ligand environment to include various polydentate amine ligands. We report here the acid decomposition of (pyridylmethyl)chromium(III) complexes containing the amine ligands 1,3-diaminopropane (dap), diethylenetriamine (dien), triethylenetetramine (trien), and 1,4,8,12-tetraazacyclopentadecane ([15]aneN$_4$). The results obtained are correlated with those for the related ethylenediamine (en)[10] and aquo (H_2O)[12,19] complexes.

Experimental Section

Perchloric acid was BDH AR grade, sodium perchlorate was Merck reagent grade. Diethyl ether and methylene chloride were BDH AR grade. The organochromium complexes **1–4** were prepared and isolated as previously reported.[1,11]

UV spectra were recorded on a Beckman 5270, a Varian Superscan or a Cary 17 instrument in stoppered, 1-cm cuvettes. The cell holders were thermostated to ±0.1 °C with a Haake circulating-water thermostat.

The mass spectra were obtained by using a Kratos AEI MS3074 double-beam, high-resolution GC-mass spectrometer. Samples were separated on the same column used for gas chromatographic analyses. Data acquisition was done with a NOVA-3 minicomputer.

Gas chromatography was carried out on a Varian Autoprep or a Hewlett-Packard HP 5840A gas chromatograph with flame-ionization detectors. A 5-ft stainless-steel column packed with 5% SE-30 on Chromasorb W was used. A head pressure of 8 psi of He was used for the separation of amine, picoline, pyridine, and aldehyde under isothermal conditions at 60 °C while separation of the higher boiling compounds was achieved by using a head pressure of 10 psi He and programming the temperature from an initial temperature of 75 °C at a rate of 0.25° min^{-1} for 2 min followed by 16° min^{-1} to a maximum temperature of 180°.

The NMR spectra were measured on an Hitachi Perkin-Elmer R-20B high-resolution spectrophotometer.

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Table I. Rate Constants for Decomposition of 3-py$CH_2Cr^{III}(L)_x$ Ions in 1 M $HClO_4$

L	t, °C	10^4k_1, s^{-1}	10^4k_2, s^{-1}
dap	44	3.56 ± 0.09	0.555 ± 0.02
	45.8	3.74 ± 0.10	0.976 ± 0.005
	48.4	5.29 ± 0.37	1.19 ± 0.004
	50	5.89 ± 0.09	1.72 ± 0.02
	54.2	10.80 ± 0.53	3.56 ± 0.02
		11.69 ± 1.23	3.40 ± 0.20[b]
	55	9.15 ± 0.28	4.00 ± 0.25
		3.56 ± 0.60	3.94 ± 0.19[a]
	60.5	20.85 ± 0.27	9.35 ± 0.18
		20.19 ± 0.96	10.44 ± 0.11[a]
		16.08 ± 0.26	9.86 ± 0.56[b]
	66.2	42.39 ± 2.55	16.10 ± 0.27
dien	45	1.32 ± 0.01	0.418 ± 0.004
	50	7.88 ± 0.44	0.898 ± 0.005
	55.2	10.06 ± 0.62	1.61 ± 0.02
	60	19.33 ± 0.67	2.743 ± 0.02
	65	102.5 ± 9.7	5.384 ± 0.09
trien	44.5	3.22 ± 0.11	1.19 ± 0.03
	49.8	4.86 ± 0.12	1.91 ± 0.02
	59.2	16.33 ± 1.01	6.81 ± 0.09
[15]aneN$_4$	40		0.138 ± 0.002
	50.1		0.484 ± 0.008
	55		0.838 ± 0.011
	61.2		1.542 ± 0.017
en[c]	35.4		0.123
	45.2		0.490
	50.2		0.98
	55.0		2.22
	64.0		8.3
H_2O[d]	24.85		0.0022
	39.95		0.339 ± 0.007
	50.2		1.94 ± 0.04
	55.0		4.33 ± 0.09

[a] 0.01 M $HClO_4$. [b] 0.1 M $HClO_4$. [c] Reference 10. [d] Reference 19.

The kinetics of decomposition were followed under aerobic conditions for ~10^{-4} M solutions of the isolated organochromium complexes in perchloric acid with the ionic strength maintained at 1.0 M with sodium perchlorate. Absorbance vs. time plots at or close to the absorbance maximum of the organochromium species in each case were recorded at various temperatures.

Product analyses were done by using 10–15 cm^3 of ~0.5 M solutions of organometallic complexes in 2–4 M perchloric acid. These solutions were allowed to decompose at 60 °C for about 24 h under an atmosphere of nitrogen in stoppered flasks or under an aerobic atmosphere with water-saturated air bubbling through the solution. On completion of the decomposition as determined from the absorption spectrum, the solution was basified to pH 11 with NaOH pellets and sodium carbonate. Solids that precipitated were separated from the mother liquor by centrifugation. These solids and the mother liquor were repeatedly extracted with ether and/or methylene chloride, with the extraction being followed spectrally. The extract volume was reduced by distillation, and the residue was made up to volume for quantitative analysis.

Results

1,3-Diaminopropane Complexes. The absorbance maximum of the 2-$NC_5H_4CH_2Cr(dap)_2(H_2O)^{2+}$ ion (**1a**) shifted from 322 to 320 nm and thence to 318 nm, the absorption maximum of the pentaaquo(2-pyridylmethyl)chromium(III) ion,[12] before decreasing (Figure 1a). Repetitive UV scans of the decomposition of the 3-isomer of the complex (**1b**) in 1 M $HClO_4$ showed that there was an initial shift of λ_{max} from 285 to 283 nm followed by the decrease at that wavelength (Figure 1b). Such shifts had been observed previously with the analogous ethylenediamine complexes,[10] and their significance will be discussed later. The typically curved semilog plots of $A_t - A_\infty$ at 285 nm vs. time for the 3-isomer as given in Figure 2 are indicative of consecutive reactions

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

The respective rate constants were determined from such data by using the method outlined by Wilkins.[13] The first-order rate

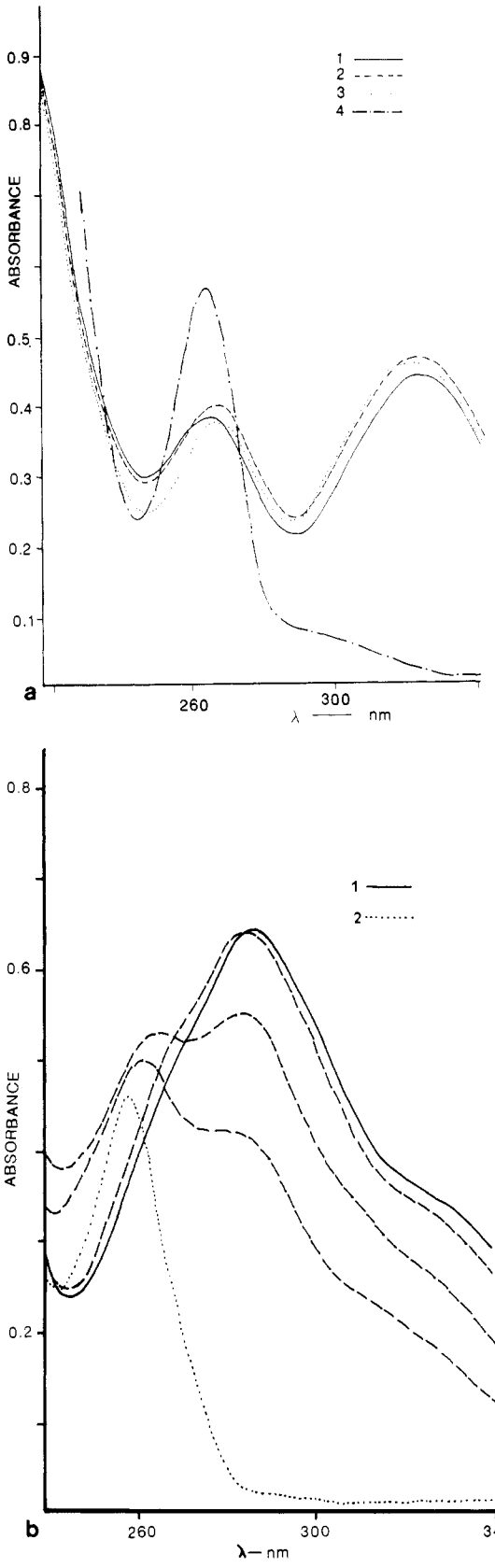

Figure 1. (a) Spectral changes for the decomposition of the 2-$pyCH_2Cr(dap)_2$ ions in 1 M $HClO_4$: (1) initial spectrum; (2) spectrum after $^1/_2$ h at 30 °C; (3) spectrum after 36 h at 30 °C; (4) product spectrum after complete decomposition at 60 °C. (b) Repetitive scan for the decomposition of 3-$pyCH_2Cr(dap)_2$ ions in 1 M $HClO_4$: (1) initial spectrum; (2) final product spectrum.

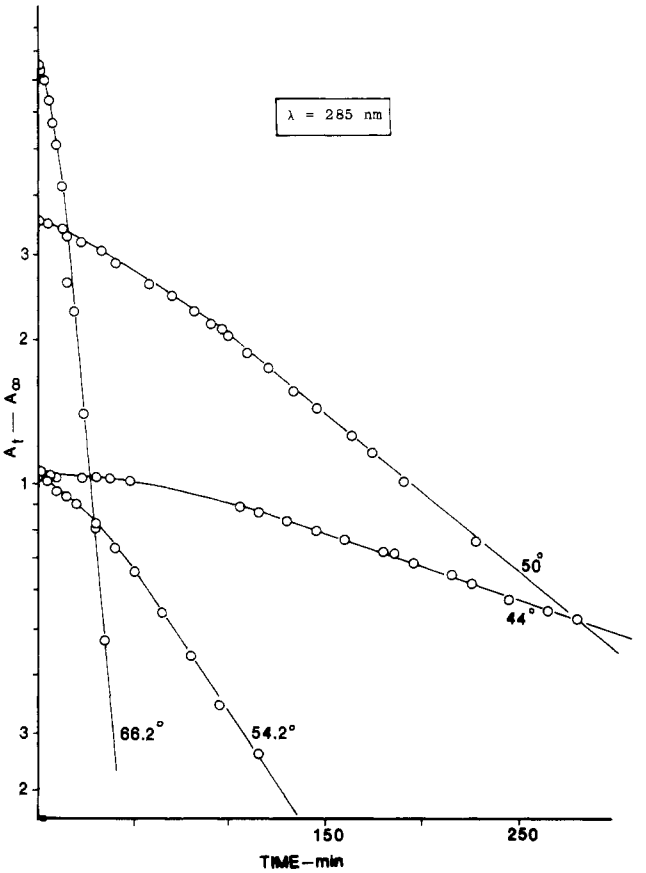

Figure 2. Semilog absorbance vs. time plots for the decomposition of the 3-$pyCH_2Cr(dap)_2$ ions in 1 M $HClO_4$ at various temperatures.

Table II. Rate Constants for Decomposition of 2-$pyCH_2Cr^{III}(L)_x$ Ions in 1 M $HClO_4$

	aquation			Cr–C cleavage	
L	t, °C	10^4k_1, s^{-1}	10^4k_2, s^{-1}	t, °C	10^4k_3, s^{-1}
dap	26	10.3 ± 0.3	1.26 ± 0.05	44	0.034 ± 0.02
				54	0.115 ± 0.001
dien	27	13 ± 1		27	0.023 ± 0.002
trien	26	5.3 ± 0.1	1.2 ± 0.1	60.4	0.269 ± 0.004
				68	1.201 ± 0.050
en[a]	27	~6	~1	55.0	0.160
				75.2	4.33
$[15]aneN_4$				60	0.252 ± 0.003
				64.8	0.535 ± 0.006
				71.6	1.338 ± 0.012
H_2O[b]				55	0.144 ± 0.003

[a] Reference 10. [b] Reference 19.

constant for the slower stage was determined in the usual manner, and the plot was extrapolated back to zero time. The logarithm of the difference between the extrapolated straight-line portion and the experimental curve was then plotted vs. time. The resultant straight line yielded the rate constant for the faster stage. An example is illustrated in Figure 3 for the decomposition of the 3-$NC_4H_5CH_2Cr(dap)_2$ ions. Kinetic data are given in Table I. As in the case of the 2- and 3-$NC_4H_5CH_2Cr(en)_2$ complexes,[10] it was observed that the rate constants were not significantly affected by a 100-fold difference in [$HClO_4$] over the range investigated, at both 55 and 61 °C. Hence subsequent studies were done in *1 M $HClO_4$ only.*

Activation parameters calculated for the 3-isomer by using the Eyring relationship are given in Table III.

The rate constants for the first two stages in the decomposition of the 2-$NC_4H_5CH_2Cr(dap)_2$ complex in 1 M $HClO_4$ are given in Table II. It is noteworthy that these rate constants are of the same order of magnitude as the estimates for the corresponding stages in the decomposition of the bis(ethylenediamine) complex.[10]

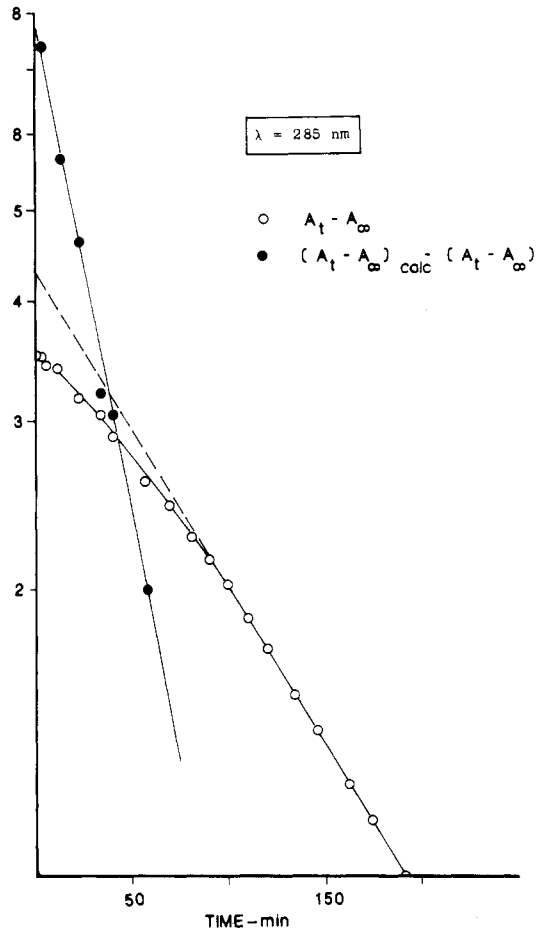

Figure 3. Semilog absorbance vs. time plots showing the separation of rate constants for the biphasic decomposition of 3-$pyCH_2Cr(dap)_2$ ions in 1 M $HClO_4$.

Table III. Activation Parameters for Decomposition of *n*-$pyCH_2Cr(L)_x$ Ions

		aquation		Cr–C cleavage		
L	*n*	$\Delta H^\ddagger$, kJ/mol	$\Delta S^\ddagger$, J/mol	$\Delta H^\ddagger$, kJ/mol	$\Delta S^\ddagger$, J/mol	ref
dap	3	99 ± 5	11 ± 16	133 ± 6	107 ± 18	*a*
diene	3	183 ± 21	267 ± 64	108 ± 3	24 ± 10	*a*
trien	3	96 ± 12	2 ± 39	103 ± 11	15 ± 36	*a*
$[15]aneN_4$	3			97 ± 2	−17 ± 8	*a*
	2			134 ± 4	81 ± 13	*a*
en	3			128 ± 5	71 ± 5	10
	2			154 ± 5	126 ± 20	10
H_2O	3			139 ± 5	109 ± 20	19
	2			156 ± 5	126 ± 20	19

[a] This work.

The rate of the Cr–C bond cleavage in the 2-isomer was very slow at 26 °C and was therefore determined at higher temperatures.

Diethylenetriamine Complexes. The decomposition of the 3-$NC_4H_5CH_2Cr(dien)$ ions (**2b**) was studied at various temperatures in *1 M $HClO_4$ only*, for the reasons stated above. (Although the species analyzed for $[pyCH_2Cr(dien)]Cl_2 \cdot 2.3HCl$ in the solid state,[1] the most probable species present in solution would be a six-coordinated $^+HpyCH_2Cr(dien)(H_2O)_x^{3+}$ ion.) Curved semilog plots of $A_t - A_\infty$ at 285 nm vs. times were also obtained indicating that the mono complex $(dien)(3\text{-}NC_5H_4CH_2)Cr$, like the bis complexes of en[10] and dap discussed above, is undergoing some degree of aquation or rearrangement prior to Cr–C scission. The rate constants, k_1 and k_2, determined in the same manner as those for the bis(1,3-diaminopropane) complexes and given in Table I again indicate two distinct stages. Activation parameters, which were calculated by using the Eyring relationship, are given in Table III.

Table IV

		product yield, %	
L	atm	picoline	1,2-dipyrid-3-ylethane
dien	N_2	55	30
	O_2	48	38
trien	N_2	58	30
	O_2	51	34
dap	N_2	65	20
	O_2[a]	11	38

[a] This reaction also included an incompletely characterized product (37%), the mass spectrum of which indicated the presence of an amine and two pyridylmethyl groups.

The spectral changes clearly indicated only one aquation step prior to decomposition in the case of the 2-pyridylmethyl isomer. The rate constants are given in Table II.

Triethylenetetramine Complexes. The $NC_5H_4CH_2Cr(trienHCl)_2$ ions (**3a** and **3b**) also underwent stepwise decomposition in 1 M $HClO_4$. An initial shift in absorption maximum from 285 to 283 nm was followed by a reduction in absorbance at 283 nm accompanied by an increase in absorbance at 263 nm consistent with the formation of organic picolyl products. The semilog plots for $A_t - A_\infty$ at 285 nm vs. time were curved, and the treatment outlined above gave rate constants for the initial step and the slower second stage. Rate constants for 44.5, 49.8, and 59.2 °C are given in Table I. The activation parameters are given in Table III.

It was apparent from the series of scans for the decomposition of the $2\text{-}NC_5H_4CH_2Cr(trienHCl)_2$ that this complex, like all the other amine complexes of this 2-isomer discussed thus far, underwent aquation to the pentaaquo complex prior to Cr–C bond cleavage. The absorption maximum shifted from 329 to 327 nm and then to 318 nm. The rate constants are given in Table II.

Tetraazacyclopentadecane Complexes. No shift in λ_{max} was observed in the acid decomposition of either the 2- or 3-complex ions. The straight-line semilog plots also indicated a single-stage direct cleavage of the Cr–C bond without prior aquation. The rate constants obtained are given in Table I and Table II while the activation parameters are given in Table III.

Products. The character of the organic products in the kinetic runs were indicated by the UV spectra of the decomposed solutions, λ_{max} = 259 nm for the 3-isomer and λ_{max} = 258–269 nm for the 2-picolyl isomers. On removal of the inorganic products *via* ion exchange on a Bio-Rad AG50-W8X column all these solutions showed λ_{max} = 263 nm, which corresponded most closely to the maxima for the methylpyridines.

The products which were highly soluble in water were of necessity isolated from solutions having concentrations of the organometallic complexes 1000-fold greater than those used in the kinetic runs. However, it is pertinent to point out here that the spectral characteristics of diluted samples of these decomposed solutions were found to be identical with those from the kinetic runs in all cases. A complete products analysis was not done for the 2-isomers containing the dap, dien, or trien ligands since these isomers all decomposed via the pentaaquo(pyridylmethyl)chromium complex for which the products had already been determined.[10] However, free amine was detected for all of these 2-isomers as for the 3-isomers. The organic products obtained when the 3-isomer was decomposed are given in Table IV.

No products were isolated for the complexes containing the macrocycle because only comparatively dilute solutions were obtained in the preparative stage.[1]

Discussion

Rate Studies. The values of kinetic parameters for the Cr–C bond cleavage in the 3-isomer of the dap complex (**1b**) closely resemble those for the corresponding pentaaquo ion. In general, positive values for the activation entropy have been interpreted from a mechanistic viewpoint as being an indication of relative freedom in the transition state. For the chromium complexes, therefore, positive values of $\Delta S^\ddagger$ have been taken as being characteristic of homolytic dissociation while negative values

indicate heterolysis.[14-19] The high $\Delta H^{\ddagger}$ values are also expected for an unassisted homolytic bond-breaking process, as found for other organochromium and organocobalt complexes.[20] Therefore, we have here another example of a homolytic Cr–C bond cleavage.

The proximity of the rate of the Cr–C bond cleavage in the 2-isomer of the dap complex (**1a**) to those of the 2-py$CH_2Cr(H_2O)_5$ complex ions[19] together with the spectral evidence above for the formation of the pentaaquo(pyridylmethyl)chromium ions prior to Cr–C bond cleavage indicates that complete stepwise aquation of the 1,3-diaminopropane complex most probably occurs via eq 1 and 2 before scission of the Cr–C bond, eq 3. Similar observations have been reported for the 2-$NC_5H_4CH_2Cr(en)_2$ complex.[10]

$$^{+}HpyCH_2Cr(dap)(H_2O)^{2+} + 2H_2O \rightarrow {}^{+}HpyCH_2Cr(dap)(H_2O)_3^{2+} + dap \quad (1)$$

$$^{+}HpyCH_2Cr(dap)(H_2O)_3^{2+} + 2H_2O \rightarrow {}^{+}HpyCH_2Cr(H_2O)_5^{2+} + dap \quad (2)$$

$$^{+}HpyCH_2Cr(H_2O)_5^{2+} \rightarrow {}^{+}HpyCH_2\cdot + Cr(H_2O)_5^{2+} \quad (3)$$

In the case of the 3-py$CH_2Cr(dap)_2$ complex the initial shift in absorption maximum from 285 to 283 nm is followed by the decrease in absorbance at 283 nm with an accompanying increase in absorbance at 259 nm. The absorbance at 259 nm is characteristic of 3-pyridyl organic products resulting from the cleavage of the Cr–C bond. It is noted that λ_{max} = 283 nm is not the spectral characteristic of 3-py$CH_2Cr(H_2O)_5^{2+}$ (λ_{max} = 285 nm in acid).[12] Hence it is apparent that the 3-isomer of the dap complex does not decompose via its fully aquated derivative as in the case of the 2-isomer. Instead it is most probable that k_1 also corresponds to an aquation step (eq 1) and k_2 corresponds to the bond cleavage step as represented by eq 4.

$$^{+}HpyCH_2Cr(dap)(H_2O)_3^{2+} \rightarrow {}^{+}HpyCH_2\cdot + Cr(dap)(H_2O)_3^{2+} \quad (4)$$

The shift in absorbance maximum of the 2-pyCH_2Cr(dien) isomer directly from 323 to 318 nm at 27 °C would suggest that the dien ligand is lost in one step, eq 5, or that the dien ligand

$$2\text{-}{}^{+}HpyCH_2Cr(dien)(H_2O)_x^{2+} + nH_2O \rightarrow 2\text{-}{}^{+}HpyCH_2Cr(H_2O)_5^{2+} + dien \quad (5)$$

is protonated to some degree. Alternatively, it may also simply be a case in which the number of aquation steps is not accurately reflected by the number of spectral shifts. The rate constant determined for the subsequent Cr–C cleavage at 27 °C, 2.25 ± 0.22 × 10^{-6} s^{-1}, is comparable, as expected, to that for the pentaaquo complex under similar conditions.

In the case of the 3-pyCH_2Cr(dien) ion (**2b**) the degree of aquation is not apparent from the spectral changes as both the dien and the pentaaquo species possess identical absorption maxima (λ_{max} = 285 nm) in their UV spectra. However, the semilog plot is curved, enabling the rate constant for the aquation as well as that for the Cr–C cleavage to be calculated. The value of k_2 at 55.2 °C (1.61 × 10^{-4} s^{-1}), which is identified with the Cr-C cleavage, is significantly different from the rate constant (4.33 × 10^{-4} s^{-1}) at 55.0 °C for the pentaaquo species,[19] which indicates that the complex does not fully aquate to the pentaaquo species prior to the Cr-C bond cleavage, eq 6.

$$3\text{-}{}^{+}HpyCH_2Cr(dien)(H_2O)_x^{2+} + nH_2O \rightarrow 3\text{-}{}^{+}HpyCH_2Cr(dien)(H_2O)_{x+n}^{2+} \quad n \leq 2 \quad (6)$$

In analogy with the other amine complexes discussed so far, the faster initial stage in the decomposition of the 3-pyCH_2Cr(trien) complex was probably associated with a partial aquation involving the trien ligands since the kinetics of the subsequent Cr–C bond cleavage is different from that of the pentaaquo ion. The aquation process is most probably accompanied or followed by rearrangement of the trien ligands as was manifested at lower temperatures, for example, at 27 °C where the complicated nature of the absorbance vs. time plot for the earlier stages must have arisen from overlapping aquation and/or rearrangement steps as the stepwise cleavage of the multidentate ligand[21] occurred.

There is a noteworthy contrast in the manner in which the tetraaza[15]ane complexes decompose in acid. Whereas the 2- and 3-isomers with the dap, en, dien, and trien ligands undergo complete and partial aquation, respectively, prior to Cr–C bond cleavage as discussed above, both the 2- and 3-pyridylmethyl isomers of the [15]aneN_4 complex go through a one-step decomposition involving the Cr–C bond cleavage without any prior aquation of the macrocyclic ligand.

The decomposition products lend further support to a decomposition mechanism based upon homolysis as suggested by Coombes and Johnson[19] and Schmidt and Swaddle[22] in preference to a heterolytic process via a carbonium ion. A carbonium ion intermediate would be expected to lead to (pyridylmethyl)carbinols as major products, and these were not detected. Decomposition via a carbanion might also be considered since the methylpyridines could possibly be derived from such a reaction. However, under the experimental conditions employed, the most plausible mechanism would be the homolytic pathway, the reverse of the well-documented mechanism of formation.

It has been shown by Kirker, Bakac, and Espenson[23] that, by selection of reaction conditions and the addition of other reagents, a particular decomposition route, homolysis or heterolysis, could be made to dominate for nearly every organochromium system studied. In most cases the homolytic process occurs more rapidly than the heterolytic, but since the homolysis is actually an equilibrium process, it can be suppressed by addition of Cr^{2+} ions, one of the products. As was pointed out by the authors, however, the heterolytic cleavage of the Cr-C bond does not necessarily suggest that the process is a dissociative one, producing a free carbanion, which would not be expected to exist in such solutions because of its basicity. Rather, the mechanism would involve nearly complete formation of the C–H bond in the transition state followed by reaction with a coordinated water molecule rather than the bulk solvent. As expected, addition of a chemical scavenger for the homolysis fragments was reported to prevent their recombination, thus enabling the homolysis to go to completion.

Thus, homolysis as represented by eq 7 followed by processes similar to those suggested by Coombes and Johnson[19] as represented by eq 8 and 9 are expected to occur. In each case, the

$$^{+}HpyCH_2\text{–}Cr(L)^{2+} \rightarrow (HpyCH_2)^{+} + Cr^{II}(L)^{2+} \quad (7)$$

$$^{+}HpyCH_2\cdot + [H_2O\cdot Cr(H_2O)_4]^{2+} \rightarrow {}^{+}HpyCH_3 + [HOCr(H_2O)_4]^{2+} \quad (8)$$

$$[HOCr(H_2O)_4]^{2+} + {}^{+}H_3O \rightarrow [Cr(H_2O)_6]^{3+} \quad (9)$$

picolines produced here most probably arose from hydrogen abstraction from the ligated amine by the radical within the solvent cage immediately following the cleavage of the bond. That hydrogen abstraction does not come from the solvent medium is clearly demonstrated in studies on the benzylchromium species to be discussed in a further publication.

Reaction of the radical with dissolved oxygen would lead to aldehydes and/or acids as products. The absence of these oxygen-containing products among those detected in this work would seem to indicate that the pyridylmethyl radical can rapidly abstract hydrogen in the solvent cage before it encounters any O_2 molecules. However, it is clear that the presence of oxygen does play a role in the determination of the relative proportions of the various products. If the acidolysis of the Cr-C complexes is indeed homolytic, the decomposition rate and the products should be affected

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Table V. Rate Parameters for Aquation of Cr(III) Aquo Amine Complexes at 60 °C

complex	$[HClO_4]$, M	k, s^{-1}	ref
$1,2,6\text{-}Cr(trienH)(H_2O)_3^{4+}$	2	1.2×10^{-3}	27
$1,2,3\text{-}Cr(trienH)(H_2O)_3^{4+}$	2	$<1.3 \times 10^{-4}$	27
$Cr(trienH_2)(H_2O)_4^{5+}$	2	3.07×10^{-5}	27
$Cr(trienH_3)(H_2O)_5^{6+}$	2	2.08×10^{-6}	27
$3\text{-}HpyCH_2Cr(trienH_n)(H_2O)_{n+1}^{(3+n)+}$	1	1.6×10^{-5}	this work
$1,2,6\text{-}Cr(dien)(H_2O)_3^{3+}$	1	1.6×10^{-2}	24
$1,2,3\text{-}Cr(dien)(H_2O)_3^{3+}$	1	5.89×10^{-5}	24
$Cr(dienH)(H_2O)_4^{4+}$	1	2.16×10^{-5}	24
$Cr(dienH_2)(H_2O)_5^{5+}$	1	2.6×10^{-6}	24
$3\text{-}HpyCH_2Cr(dienH)(H_2O)_3^{4+}$	1	1.93×10^{-5}	this work
$trans\text{-}[Cr(en)_2(H_2O)Cl]^{2+}$ [a]	0.1	4.2×10^{-5}	30
$Cr(en)(H_2O)_4^{3+}$	3	3.0×10^{-6}	29
$Cr(enH)(H_2O)_5^{4+}$	3	1.9×10^{-6}	29
$3\text{-}HpyCH_2Cr(dap)_2(H_2O)^{3+}$	1	2.09×10^{-5}	this work

[a] For the aquation to $[Cr(en)(H_2O)_3Cl]^{2+}$ at 35 °C.

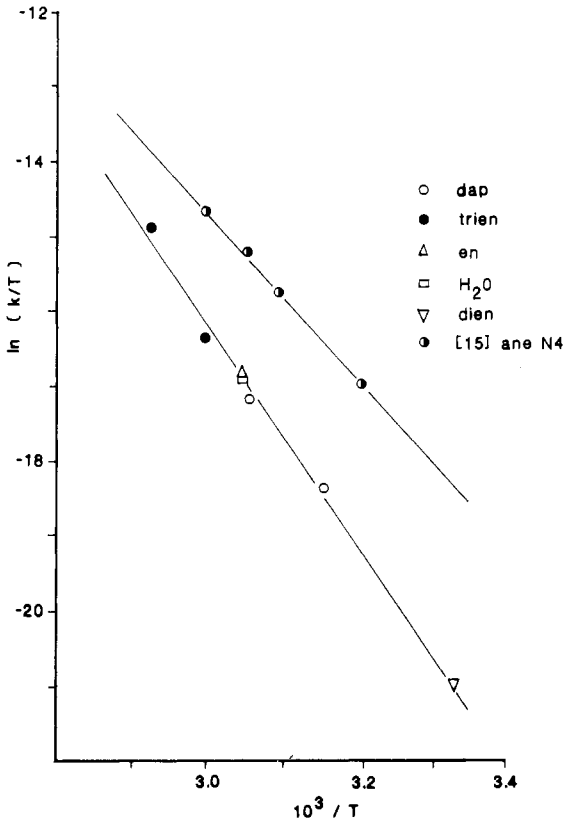

Figure 4. Eyring plot for the Cr–C bond cleavage in the various 2-$pyCH_2Cr(amine)_n$ ions in 1 M $HClO_4$.

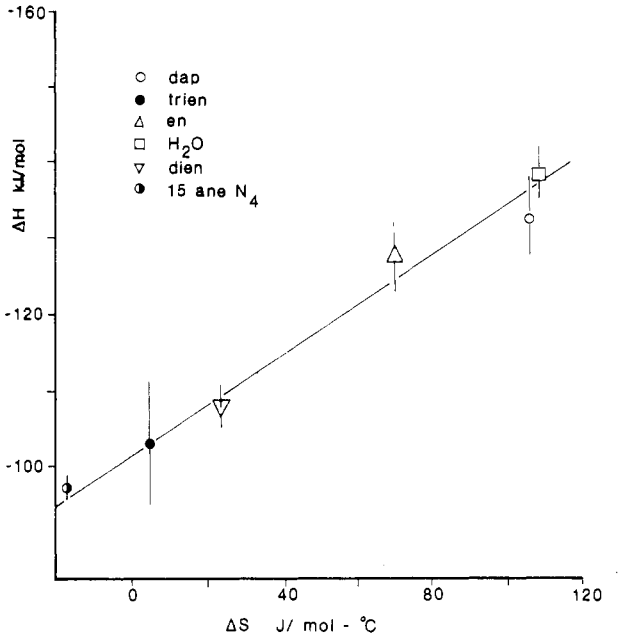

Figure 5. Isokinetic plot for the Cr–C bond cleavage in the various 3-$pyCH_2Cr(amine)_n$ ions in 1 M $HClO_4$.

by the presence of oxygen, because the pyridiomethyl radical reacts very rapidly with chromous ion and the latter would be removed from the system by oxygen. It must also be noted that if the pyridylmethyl radical is present in sufficiently high concentrations it may be able to attack the (pyridylmethyl)chromium ion to give dimeric products perhaps via an unstable (dipyridiniomethyl)-chromium ion. This, of course, does not preclude the possibility of dimerization of the pyridiniomethyl radical in the relatively concentrated solutions used in this study.

An Eyring plot for the various 2-picolyl isomers is given in Figure 4 for the Cr–C cleavage based upon the data given in Table IV. It is apparent that the points for each sample, except that containing the macrocyclic ligand, fall on the same line. This lends further support to the proposal that the complexes other than those containing the macrocyclic ligand undergo aquation to the pentaaquo(pyridylmethyl)chromium complex before Cr–C scission.

An isokinetic plot for the second stage of the decomposition of the 3-pyridylmethyl complexes, which has been assigned to the Cr-C cleavage, is given in Figure 5. A closely related series of reactions for which a common mechanism and rate-determining step is proposed should have parallel changes in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.[24] The linear relationship shown in the plot in Figure 5 supports the conclusion that Cr–C scission in these complexes proceeds via a like mechanism in each case. The isokinetic temperature determined for this series is 60 ± 5 °C.

With the exception of the $3\text{-}NC_5H_4CH_2Cr([15]aneN_4)$ complex, all activation entropies determined in this work are highly positive, indicating that the Cr–C cleavage is homolytic. Although $\Delta S^{\ddagger}$ was found to be negative in the case of the complex containing the macrocyclic ligand, its value is small compared to those reported for heterolytic cleavage in other organochromium complexes; for example, for $C_5H_9Cr(H_2O)_5^{2+}$, $\Delta S^{\ddagger} = -61.5 \pm 7.9$ J/(mol deg),[18] and for $C_6H_5CH_2Cr(H_2)_5^{2+}$, $\Delta S^{\ddagger} = -58$ J/(mol deg).[14] Therefore, the negative activation entropy is probably not indicative of an heterolytic pathway in this case. This conclusion is further supported by the fact that its activation parameters fit the isokinetic plot.

Finally, a comparison is made of the initial aquation rates in the decomposition of both the 2- and 3-pyridylmethyl complexes containing those ligands other than the macrocyclic ligand with the aquation parameters of related inorganic aquoamine complexes that have been determined by Garner and co-workers.[25-28] Data

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are available for the trien, dien, and en ligands. These are reproduced in Table V. The k_1's at ~60 °C reported here for the dien and trien 3-isomer complexes are close to the rate constants determined by Garner et al. for the intermediate aquation steps of the related inorganic complexes. It therefore appears that, whether or not the Cr is bonded to carbon, the rate constants for the aquation steps do not differ very much. It may be expected that the Cr–C cleavage in the 3-isomers (average $k \sim 5 \times 10^{-4}$ s^{-1} at 60 °C) occurs before the loss of all amine ligands because the rate constants for the final aquation steps are at least 1 order of magnitude slower than that of the Cr–C cleavage. Conversely, as is seen from Table II, in the case of the 2-isomers, complete aquation precedes the Cr–C bond cleavage, which is 2–3 times slower than the aquation steps. By comparison, the complexes containing macrocyclic ligands are considerably more stable than those containing straight-chain amine ligands—the macrocyclic effect.[29,30] Therefore, by analogy, the macrocyclic complex would be expected to undergo Cr–C cleavage with the Cr–N linkages in the complex remaining intact, and this was indeed observed. However, the ultimate reason for the faster cleavage of the Cr–C bond in the 3-isomer as compared to the 2-isomer is still unclear and is under continuing investigation.

Acknowledgment. The authors thank the University of Malaya and the University of Agriculture, Malaysia (K.C.), for financial support and Prof. A. G. Sykes for helpful discussions.

Registry No. **1a**, 99725-95-8; **1b**, 99725-96-9; **2a**, 99708-64-2; **2b**, 99708-65-3; **3a**, 99708-66-4; **3b**, 99708-67-5; **4a**, 99708-68-6; **4b**, 99708-69-7; 3-$HpyCH_2Cr(dienH)(H_2O)_3^{4+}$, 99708-70-0; 3-$HpyCH_2Cr(dap)_2(H_2O)^{3+}$, 99708-71-1; 3-picoline, 108-99-6; 1,2-dipyrid-3-ylethane, 4916-58-9.

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Hydrolysis of Coordinated Trifluoromethanesulfonate from Cobalt(III), Rhodium(III), Iridium(III), and Chromium(III) Pentaamines

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Received July 17, 1985

Base hydrolysis and aquation of $M(NH_3)_5(OSO_2CF_3)^{2+}$ (M = Co, Rh, Ir, Cr) and $M(NH_2CH_3)_5(OSO_2CF_3)^{2+}$ (M = Co, Rh, Cr) complexes at 25 °C and I = 1.0 M are reported. N-Methylation of the ammine ligand causes a marked enhancement of the rate of base hydrolysis reactions with k_{Me}/k_H of $>10^3$ (Co), 150 (Rh), and 800 (Cr). Only minor enhancements occur for aquation with Co and Rh, while there is a minor rate diminution with Cr. Positive activation entropies for base hydrolysis of $M(NH_3)_5(OSO_2CF_3)^{2+}$ (M = Co, Ir) and competition experiments with azide ion in basic solution as well as the absence of the competing ion in the rate law allow a dissociative conjugate-base mechanism for all complexes. The variation in rate enhancement from ammine to methylamine compounds and the competition studies in base with azide ion chiefly reflect differences in steric interactions due to differing metal–ligand bond lengths rather than any mechanistic diversity. Variations in competition behavior for rhodium(III), chromium(III), and cobalt(III) appear to reflect relative lifetimes of the intermediate of reduced coordination number. The variations in aquation are much smaller and do not allow any certainty in mechanistic assertions. Marked accelerations of rates for both acid and base hydrolyses (~10^3–10^6-fold) occur consistently for all trifluoromethanesulfonato complexes compared with those of halo analogues.

Introduction

Studies of hydrolysis reactions of amine complexes of inert d^3 (Cr^{III}) and d^6 (Co^{III}, Rh^{III}, Ir^{III}) ions have an extensive and venerable history, and this research has been widely reviewed.[3-6] Despite this activity, mechanistic aspects still need to be resolved. Overall, aquation reactions of the cobalt(III) complexes appear to be largely dissociative in nature; i.e., bond breaking substantially leads bond making. However, for chromium(III) complexes, more associative character appears to be evident.[7] The rate enhancement observed for cobalt(III) when the nonleaving groups are changed from pentaammine to pentakis(methylamine) with concomitant increase in steric strain contrasts with a rate reduction at chromium(III) in the same circumstances.[8,9] It can be argued that this is consistent with the assessment above. With rhodium(III), the effect is not so significant, and arguments[7] about the degree of associative character in that case are more tenuous. For base hydrolysis, a conjugate-base mechanism seems well-defined, although whether a limiting dissociative process (S_N1CB) obtains universally for these elements is more doubtful.[3,4]

Syntheses of labile trifluoromethanesulfonato ($-OSO_2CF_3$) complexes of inert d^3 and d^6 metal amines have been reported recently;[10-12] the Co(III) complexes aquate rapidly compared with their halo analogues and approach perchlorato complexes in lability.[13] In base, hydrolysis is even more rapid. Reactivity studies of the more kinetically inert metal ions such as Cr(III), Rh(III), and Ir(III) therefore become readily accessible if good leaving groups such as $CF_3SO_3^-$ are used. Here, we report the base

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