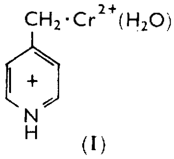
σ-Bonded Organotransition-Metal Ions. Part II.[1] Kinetics and Mechanism of the Aerobic Acidolysis of Penta-aquo(pyridiomethyl)chromium(III) Ions

By R. G. Coombes and M. D. Johnson

The kinetics of the acidolysis of the three penta-aquo(pyridiomethyl)chromium(III) perchlorates have been studied in from 5·5M to 2×10^{-3}M perchloric acid, with and without added lithium perchlorate, in the presence of air. The uncatalysed reaction, which is evident in the range 0·2—0·002N-acid in the absence of added salt, involves the homolytic dissociation of the carbon–chromium bond, the reverse of which is largely prevented by the oxidation of chromous ion with air. The products and activation parameters are consistent with the formation of the pyridiomethyl radicals, and it is possible that a proportion of these radicals may also attack the pyridiomethylchromium ions. The acidolysis is catalysed by higher concentrations of perchloric acid or lithium perchlorate without changing the mechanism, but an even greater acceleration by sodium acetate is due to a change in mechanism. In all cases, in the presence of air, good first-order kinetics were observed.

THE first Paper in this Series [1] described the preparation and characterisation of the air-stable penta-aquo-(pyridiomethyl)chromium ions (I, II, and III). The stability of these ions in air has enabled us to carry out detailed studies on their reactions with a view to obtaining information as to the properties of carbon–chromium bonds. The main interest is in the comparison of these ions with other corresponding carbon–metal compounds and penta-aquochromium(III) complexes.

Preliminary experiments had shown that the decomposition of these compounds is accelerated by strong bases, strong acids, some metal halides, nucleophiles, and chromous ion. Since other workers have observed acid catalysis in the hydrolysis of organometallic compounds, such as organomercury halides,[2] and of penta-aquochromium(III) complexes, such as penta-aquoazido-chromium(III) ion,[3] it was decided to study in detail the acidolysis of the pyridiomethylchromium ions. However, though there are a number of features, such as the high solubility of these ions and of their possible reaction products in water, which simplify consideration of these reactions, there are also a number of likely complications. One of the main problems involves the possibility of reaction of oxygen, if not with the ions themselves at high temperatures, then with intermediates in, and products of, the reaction. This might lead to complications in the kinetics and a change in the nature of the products. For example, oxygen is known to affect the rates of the acid-catalysed hydrolysis of isopropylmercuric halides [4] in perchloric acid, though they are themselves considered to be stable to oxygen. On the other hand, if oxygen were rigorously excluded, the formation of chromous ion during the reaction might lead to a significant acceleration in the rate of the decomposition of the pyridiomethylchromium ion and to different products. Indeed, Kochi and Buchanan [5] have been unable to decipher the kinetics of the acid-catalysed solvolysis of the penta-aquobenzylchromium-(III) ion in aqueous ethanolic perchloric acid in the absence of oxygen. Therefore, the work described in this paper involves reactions done in the presence of oxygen, and only brief mention is made of reactions in the absence of air.



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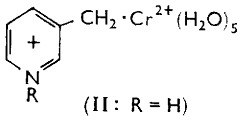
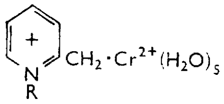


(II: R = H)
(IV: R = Me)



(III: R = H)
(V: R = Me)

RESULTS

Kinetics.—Rate measurements were made spectrophotometrically by following the change in absorbance at several wavelengths in the ultraviolet region of solutions

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

[2] M. M. Kreevoy, *J. Amer. Chem. Soc.*, 1957, **79**, 5925.

[3] T. W. Swaddle and E. L. King, *Inorg. Chem.*, 1964, **3**, 234.

[4] M. M. Kreevoy and R. L. Hansen, *J. Phys. Chem.*, 1961, **65**, 1055.

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

of the pyridiomethylchromium ions in from 0·002 to 5·5M-perchloric acid, with and without added lithium perchlorate. The main series of rate measurements were made using very low (*i.e.*, *ca.* 10^{-5}M) concentration of the complex ion. In these cases, the concentration of dissolved oxygen in the solutions was of the same order as that of the complex ion, and was kept approximately constant by having the solution in contact with the air throughout the reaction. In all cases good reproducible first-order kinetics were followed over several half lives (up to 6) and the rate coefficients so obtained were independent of the concentration (with the exception described below) or batch of the pyridiomethylchromium ion, and of the wavelength. For all three pyridiomethylchromium ions the uncatalysed reaction, which will be defined as that reaction having the minimum strictly first-order rate coefficient, was evident over the whole region 0·002—0·2M-perchloric acid in the absence of added lithium perchlorate, as shown in Tables 1—3. In more concentrated acid, or with significant quantities of added lithium perchlorate, the reaction was considerably faster. In the presence of added sodium acetate, an even greater rate-acceleration was observed (Table 4) than with lithium perchlorate.

TABLE 1

2-Pyridiomethylchromium ion (5 × 10^{-5}M)

T°C	[$HClO_4$]M	10^2k_{obs} (hr.$^{-1}$) ± 2%
55·0	0·002	3·9
55·0	0·02	3·59
55·0	0·12	3·55
55·0	1·02	5·2
55·0	2·16	8·4
55·0	3·35	14·1
55·0	4·50	28·6
55·0	5·06	41·2
55·0	5·16	45·1
63·9	4·95	123
63·9	0·02	16·0
55·0	0·04	6·7 [a]
55·0	1·02	12·3 [a]
55·0	2·70	29·0 [a]
55·0	5·05	181 [a]

[a] 2-(1-Methylpyridio)methylchromium(III).

TABLE 2

3-Pyridiomethylchromium ion (3 × 10^{-5}M)

T°C	[$HClO_4$]M	10^2k_{obs} (hr.$^{-1}$) ± 2%
39·95	0·02	7·5
39·95	0·12	7·7
39·95	1·02	12·2
39·95	2·08	20·3
39·95	3·10	32·6
39·95	3·98	52·8
39·95	4·55	67·6
39·95	5·08	92·7
39·95	5·39	114·1
24·85	1·02	0·80
24·85	4·83	6·0
55·0	0·02	105
55·0	1·02	156
39·95	0·01	6·0 [a]

[a] 3-(1-Methylpyridio)methylchromium ion.

For comparative purposes, some rate measurements were also made on the corresponding 1-methyl-2- and 1-methyl-3-pyridiomethylchromium ions (IV and V, respectively) in perchloric acid, and on the pyridiomethylchromium ions in nitric and sulphuric acids. These results are included in Tables 1—3.

TABLE 3

4-Pyridiomethylchromium ion

T°C	[$HClO_4$]M	[$LiClO_4$]M	10^2k_{obs} (hr.$^{-1}$) ± 2%
55·0	0·02		11·7 [d]
55·0	0·115		11·8 [d]
55·0	1·00		18·6 [e]
55·0	1·02		18·6 [d]
55·0	2·09		31·1 [d]
55·0	3·18		50·7 [d]
55·0	4·18		87·8 [d]
55·0	4·56		111·5 [d]
55·0	4·68		121 [d]
55·0	4·91		141 [d]
55·0	0·10	3·88	27·6 [d]
55·0	0·10	2·70	39 [d]
55·0	0·10	3·74	62·4 [d]
55·0	0·10		12·7 [a]
55·0	0·10		32 [b]
55·0	0·50		19·1 [c]
55·0	4·55		146 [c]
39·95	5·15		13·5 [d]
63·85	0·02		56·5 [d]
55·0	0·02		13·7 [f]

[a] Nitric acid. [b] Sulphuric acid. [c] 2 × 10^{-2}M complex. [d] 5 × 10^{-5}M. [e] 3 × 10^{-3}M complex. [f] 98% D_2O as solvent.

TABLE 4

4-Pyridiomethylchromium ion (1 × 10^{-5}M) in acetate buffer

T°C	[$HClO_4$]M	[CH_3COONa]M [a]	10^2k_{obs} (hr.$^{-1}$) ± 3%	$10^2k'$ (hr.$^{-1}$) [b]
55·0	0·20	0·28	7·3	3·6
40·0	0·20	0·28	1·0	0·76
25·0	0·20	0·28	0·15	0·14

[a] Stoicheiometric salt concentration. [b] Observed rate coefficient corrected for uncatalysed reaction.

Some runs were also carried out at intermediate (10^{-3}—10^{-4}M) and at high concentrations (2 × 10^{-2}M) of 4-pyridiomethylchromium ion. In the former the rate coefficients were the same as those obtained using the lowest concentrations of the substrate, but using high concentrations there was a definite increase in rate coefficient. In order to maintain the excess of oxygen at these high concentrations, it was necessary either to shake the flask with oxygen repeatedly during the runs or to bubble oxygen through the solution. These methods gave identical results; in each case good first-order kinetics were observed, and the rate coefficients for the reaction both in dilute and concentrated perchloric acid were some 30% greater than those obtained with the most dilute solutions of the 4-pyridiomethylchromium ion, as shown in Table 3.

For comparison, a run was also carried out on a concentrated solution of the 4-pyridiomethylchromium ion in 5M-perchloric acid in the presence of only limited quantities of air. In this case, first-order kinetics were not observed; the slope of the first-order plot gradually increased throughout the first three half-lives of the reaction, the initial rate being some 22% of that in the presence of oxygen, and the rate after 3 half-lives was some 55% of that in the presence of oxygen.

Activation Parameters.—Activation energies and entropies were calculated from data at two temperatures for the uncatalysed and salt-catalysed reactions of each pyridiomethylchromium ion and for the sodium acetate-catalysed reaction of the 4-pyridiomethylchromium ion. These are assembled in Table 5. In one case the activation parameters of the partially catalysed reaction in M-perchloric acid was also measured from data at three temperatures and gave an appropriate intermediate pair of values.

Products.—No products could be isolated from the most dilute solutions used for the main kinetic runs, but the ultraviolet spectra of the final solutions (Table 6) indicated that the main product from both uncatalysed and salt-catalysed reactions was the corresponding pyridine-2-, 3-, or 4-aldehyde.[6] ($\lambda_{max.}$ 259,2 58, and 256 mμ, respectively.)

TABLE 5

Activation parameters

Compound	[HClO$_4$]M	ΔH‡ ± 1·0 kcal./mol.	ΔS‡ ± 5 e.u.
2-Pyridiomethyl-chromium(III)	0·1	37·2	+30
ditto	4·95	30·4	+14
3-Pyridiomethyl-chromium(III)	0·02	35·5	+32
ditto	1·02	33·3	+26
ditto	4·83	31·3	+23
4-Pyridiomethyl-chromium(III)	0·02	39·5	+37
ditto	5·15	33·3	+26
ditto[a]	0·20	26	−6
ditto[b]	0·20	21	−21

[a] Acetate buffer, 0·28M sodium acetate. [b] Acetate buffer, 0·28M sodium acetate; after correction for the uncatalysed reaction.

TABLE 6

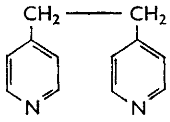
Ultraviolet spectra of reaction products

Compound	Final $\lambda_{max.}$ (mμ) (Acid decomposition)		Final $\lambda_{max.}$ (mμ) (Alkaline decomposition)
	a	*b*	
2-Pyridiomethyl chromium	259—260	260	262·5
3-Pyridiomethyl chromium	259	260—261	261[c]
4-Pyridiomethyl chromium	256—257	253	252·5

[a] 3×10^{-5}M complex. [b] *ca.* 1×10^{-3}M complex. [c] Some decomposition of stock solution before reaction in alkali.

These maxima are sufficiently different from those for the methylpyridines[7] (262·5, 262·5, and 252·5 mμ, respectively), 1,2-di-4′-pyridylethane[8] (253 mμ), pyridylmethanols[8] (261·5, 261, and 253·5 mμ, respectively), and pyridylcarboxylic acids[8,9] (266, 261, and 272 mμ) in acid solution which might have been expected as alternative products. For the reaction at intermediate concentrations the ultraviolet spectra of the final solutions (Table 6) suggest that the product might also contain the methylpyridines and dipyridylethanes. For those runs using the highest concentrations of pyridiomethylchromium ions a fair proportion of the products could be isolated, and the following discussion refers mainly to the products from the reaction of the 4-pyridiomethylchromium ion (2×10^{-2}M) which was studied in the most detail.

In 4·5M-perchloric acid, under conditions exactly analogous to those used for the rate measurements, *i.e.*, with oxygen bubbling through the solution, the main product was 1,2-di-4′-pyridylethane (45%) (VI) together with pyridine-4-aldehyde (15%) (VII), 4-methylpyridine (20%) (VIII), and some unknown products, possibly other coupled methylpyridine derivatives or material produced during the working up procedure. In 0·5M-perchloric acid the main product was pyridine-4-aldehyde (60%), 4-methylpyridine (15%), and 1,2-di-4′-pyridylethane (5%), and approximately 20% of other products. When the 4-pyridiomethylchromium ion was decomposed in 2,5M-perchloric acid in the presence of only limited quantities of air, the product isolated was mainly 4-methylpyridine (60%) and 1,2-di-4′-pyridylethane (40%). However, though the total yield of products isolated from all of these reactions was only about 30%, tests showed that the yields isolated were approximately proportional to material present in solution. The above percentage yields are therefore only approximate, but the broad trends are significant. Simiarly, 3-pyridiomethylchromium ion in *ca.* 1·5M-perchloric acid in the presence of only a limited amount of air gave 1,2-di-3′-pyridylethane and 3-methylpyridine. 2-Pyridiomethylchromium ion in 2M-perchloric acid with limited quantities of air gave 1,2-di-2′-pyridylethane (50%) 2-methylpyridine (25%) and unknown products. In 0·5M-perchloric acid and an excess of oxygen, very little product could be isolated from the 2-pyridiomethylchromium ion. This is believed to be because pyridine-2-aldehyde is rapidly oxidised to the extremely water-soluble pyridine-2-carboxylic acid.



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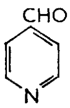

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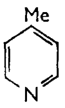
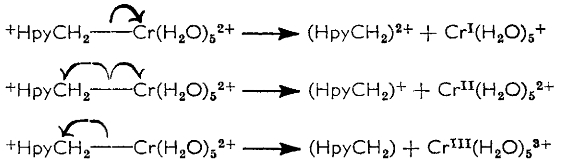


(VIII)

DISCUSSION

Uncatalysed Reaction.—The simplest modes of dissociation of the carbon–chromium bond in the pyridiomethylchromium ions would involve the formation of chromium(I), chromium(II) or chromium(III) species as shown in equations 1—3, respectively.



$$^{+}HpyCH_2—Cr(H_2O)_5^{2+} \longrightarrow (HpyCH_2)^{2+} + Cr^{I}(H_2O)_5^{+} \quad (1)$$

$$^{+}HpyCH_2—Cr(H_2O)_5^{2+} \longrightarrow (HpyCH_2)^{+} + Cr^{II}(H_2O)_5^{2+} \quad (2)$$

$$^{+}HpyCH_2—Cr(H_2O)_5^{2+} \longrightarrow (HpyCH_2) + Cr^{III}(H_2O)_5^{3+} \quad (3)$$

Equation (1) can be ruled out because the formation of chromium(I) species is most unlikely. It can also be ruled out under these conditions because the formation of pyridiniummethyl cations (*e.g.*, IX) (or pyridylmethyl cations, *e.g.*, X) would lead to significant quantities of pyridylmethylcarbinols and these cannot be found in the products at all. Equation (3) is not unlikely, but can be ruled out as the main reaction under the present conditions because the formation of 4-methylene-1,4-dihydropyridine (XII) (or the pyridylmethyl anion XI) as intermediates would lead to methylpyridine as the main product. However, as methylpyridines are formed in the reactions of the concentrated ions, this path cannot be completely ruled out.

Reaction (2) is acceptable as it is the reverse of the

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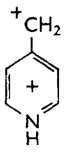
[6] K. Nakamoto and A. E. Martel, *J. Amer. Chem. Soc.*, 1959, **81**, 5857.

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

[8] R. G. Coombes and M. D. Johnson, unpublished observations.

[9] R. F. Evans, E. F. G. Hetherington, and W. Kynaston, *Trans. Faraday Soc.*, 1953, **49**, 1284.

postulated mechanism of formation of the pyridiomethylchromium ions. Moreover, the observation of 1,2-dipyridylethanes and pyridine-aldehydes in the products are certainly characteristic of the presence of pyridiomethyl (XIII) or pyridylmethyl (XIV) radicals in solution. The formation of the methylpyridines can also be accommodated on the basis of the formation of the pyridiomethyl radicals. Whilst hydrogen abstraction from water by the radicals is unlikely to take place, hydrogen abstraction from the aquated chromous ion by the pyridiomethyl radical might be possible immediately following fission of the bond and within the solvent cage, as shown in equations (4) and (5).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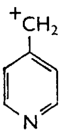
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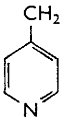
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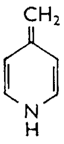
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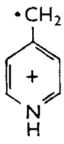
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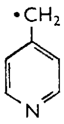

(XIV)

$$\overset{+}{\text{HpyCH}_2\cdot} + \text{H}_2\text{O}\cdot\overset{2+}{\text{Cr}(\text{H}_2\text{O})_4} \longrightarrow \overset{+}{\text{HpyCH}_3} + \overset{2+}{\text{HOCr}(\text{H}_2\text{O})_4} \quad (4)$$

$$\overset{2+}{\text{HOCr}(\text{H}_2\text{O})_4} + \overset{+}{\text{H}_3\text{O}} \longrightarrow \overset{3+}{\text{Cr}(\text{H}_2\text{O})_6} \quad (5)$$

The uniformity and reproducibility of the all kinetic results, despite the presence of oxygen, indicates that oxygen is not reacting directly with the pyridiomethylchromium ion, but the results show that oxygen does play a definite part in determining the products of the reaction. Since it is understood from the postulated mechanism of formation of the pyridiomethylchromium ions, that the reaction of the pyridiomethyl radical with chromous ion is extremely fast even at 20°, the rate of unimolecular decomposition of the pyridiomethylchromium ion will be given by equation (6).

$$-d[\text{HpyCH}_2\text{Cr}(\text{H}_2\text{O})_5{}^{3+}]/dt = k_1[\text{HpyCH}_2\text{Cr}(\text{H}_2\text{O})_5{}^{3+}] - k_{-1}[\text{HpyCH}_2{}^{+}][\text{Cr}(\text{H}_2\text{O})_5{}^{2+}] \quad (6)$$

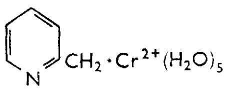
The apparent rate of reaction will therefore depend on the rate of removal of the pyridiomethyl radical and/or chromous ion from the system. Both of these species must be expected to react with oxygen, the chromous ion probably the more rapidly because the pyridiomethyl radical is likely to be more an oxidising than a reducing radical. Given a sufficiently high concentration of oxygen in the solution, the rate of the back-reaction can be substantially reduced, probably to the point where it is negligible. By this we refer only to that part of the reaction which involves species outside the immediate solvent cage, for it is assumed that even in the presence of oxygen there must be substantial recombination of the pyridiomethyl radical and chromous ion within the solvent cage.

Under these conditions, the observed first-order rate will merely represent the upper limiting rate of homolytic unimolecular dissociation of the pyridiomethylchromium ion in low concentration in the medium concerned. If this view is correct, it should be possible to explain the slight (30%) rise in rate as the concentration of the pyridiomethylchromium ion is increased to 2×10^{-2}M, and also the products obtained.

It is unlikely that the increase in rate is due to an increase in the effect of oxygen on the back-reaction, because this would imply that the back-reaction had not entirely been suppressed at the lower concentrations, and variable kinetic results would have been expected. It is also unlikely to be a salt effect (see later) and the most reasonable explanation, though only speculative, is that, after the removal of chromous ion by oxygen, the pyridiomethyl radical is sufficiently free and in a high enough concentration to attack the pyridiomethylchromium ion to give 1,2-dipyridylethane or other products, perhaps *via* an unstable dipyridiomethylchromium ion. This would lead to good first-order behaviour if the rate of attack of the pyridiomethyl radical on the pyridiomethylchromium ion were much faster than the rate of formation of the pyridiomethyl radicals. In which case the overall rate of the reaction would be given by equation (7), where x is the proportion of pyridiomethyl radicals which react with the pyridiomethylchromium ion. The upper limit to the observed rate coefficient at any particular concentration of added salt or acid would therefore be $2k_1$ (*i.e.*, where $x = 1$). The proportion of radicals reacting in this way using 2×10^{-2}M pyridiomethylchromium ion would therefore be approximately 30%. However, further discussion of this suggestion must await information about the reactivity of pyridiomethyl radicals.

$$-d[\text{HpyCH}_2\text{Cr}(\text{H}_2\text{O})_5{}^{3+}]/dt = (1 + x)k_1[\text{HpyCH}_2\text{Cr}(\text{H}_2\text{O})_5{}^{3+}] \quad (7)$$

The reversible deprotonation of one of the co-ordinated water molecules of the pyridiomethylchromium ions in the region of pH 3, which was described in Part I, does not seem to have any significant effect on the rate of the uncatalysed reaction, since the rate of the uncatalysed reaction is constant over the whole region 0·2—0·002M-perchloric acid. This behaviour is similar to that observed with penta-aquoamminochromium(III) ion, and indicates that the change of mechanism only involves the second or subsequent pK_a values. Attempts to correlate the rates measured in solutions of less than pH 3 with those in perchloric acid–sodium acetate buffers failed because of the marked change of reaction rate (and mechanism) in the presence of acetate ion and/or acetic acid. It is also clear that the reactions are not proceeding through the alternative deprotonated forms (Ia, IIa, and IIIa) of the pyridiomethylchromium ions, because the rates of reaction of the *N*-methylated pyridio-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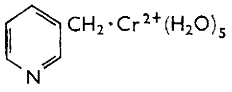
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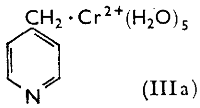
(IIIa)

methylchromium ions are of the same order as, and vary with acid concentration in a similar manner to, those of the pyridiomethylchromium ions.

Salt effects. In view of the known acid-catalysis of the hydrolysis of organomercury compounds and of azido- and fluoro-penta-aquochromium(III) ions, we initially expected that the " acid-catalysed " hydrolysis of the pyridiomethylchromium ions would show similar kinetic and product characteristics. However, it is apparent from the effect of lithium perchlorate on the rate of reaction of the 4-pyridiomethylchromium ion that the effect of added perchloric acid is a fairly large salt effect and not an acid-catalysis. The similarity of the products of the uncatalysed and salt-catalysed reaction, if not of their proportions, also suggests that the salt effect is merely a modification of the uncatalysed reaction and does not involve a change in mechanism. This is confirmed by the similarity in behaviour of the three pyridiomethylchromium ions, and the fact that the rate of reaction of more concentrated solutions of the 4-pyridiomethylchromium ion in 4·5M-perchloric acid as well as in 0·5M-perchloric acid is some 30% faster than that of more dilute solutions. It is also confirmed by the product studies discussed below.

Activation Parameters.—The activation energies and entropies for the uncatalysed reaction are extremely high, and quite different from those measured by Kochi and Buchanan[5] for the benzylchromium ion ($\Delta H^{\ddagger} = 16{\cdot}2$; $\Delta S = -13{\cdot}9$ e.u.). However, this discrepancy can be resolved when it is considered that these workers had acetate ion present in solution in order to obtain first-order kinetics. Our results show that in the presence of added acetate ion, the decomposition of the 4-pyridiomethylchromium ion is considerably accelerated, and there is a sharp fall in the activation energies and entropies to values very much closer to those described for the benzylchromium ion. Indeed, when allowance is made for the proportion of the rate coefficient which is due to the uncatalysed reactions the values are closer still to those for the benzylchromium ion (Table 5). It seems, therefore, that there is a change in the mechanism, and probably also of products, when acetate ion or acetic acid is added. This is confirmed by comparison of the very small positive solvent deuterium isotope effect (17%) observed in this work (Table 3) with the large (>400%) negative solvent isotope effect observed for the benzylchromium ion in the presence of acetate ion by Kochi and Buchanan. The significant differences between our conclusions and those of Kochi, who favours heterolytic fission of the benzylchromium ion, can largely be explained on the basis of this mechanistic difference. The high activation energy for the uncatalysed reaction is compensated for by the very high positive entropy of activation, which is characteristic of many homolytic dissociations and points to a much greater freedom in the transition state than in the initial state. On addition of perchloric acid or lithium perchlorate, the activation energy and entropy decrease significantly, possibly because the solvent cage is loosened in concentrated electrolyte solution.

This reaction has few parallels in that it involves homolytic fission with separation of the considerable charge already present in the molecule. However, there are reactions of some other penta-aquochromium (III) ions which may in fact involve the homolytic dissociation of the ligand–chromium bond in aqueous solution. For example, the uncatalysed decomposition of iodo-[10] and azido-[3]penta-aquochromium(III) ions ($\Delta H^{\ddagger} = 28$ and $32{\cdot}4$ kcal./mole, respectively; $\Delta S^{\ddagger} = 16{\cdot}4$ and $16{\cdot}2$ e.u., respectively, at unit ionic strength) have activation parameters which are similar to those described above, but quite different from those for the heterolytic dissociation of thiocyanato-,[11] bromo-,[12] chloro,-[13] and fluoro-[13] penta-aquochromium(III) ions ($\Delta H^{\ddagger} = 27{\cdot}5$, $23{\cdot}8$, $24{\cdot}3$, and $28{\cdot}7$ kcal./mole, respectively, $\Delta S^{\ddagger} = -3{\cdot}5$, $-3{\cdot}5$, $-7{\cdot}1$, and $-3{\cdot}9$, e.u. respectively). Moreover the fate of the iodine atom and azide group have not been settled, and it remains to be proved that these reaction are not also homolytic. It may also be significant that two sets of values have been reported for the activation parameters of iodopenta-aquochromium(III) ion, and the suggestion has been made that one set of values involves catalysis (perhaps inducing homolytic fission) by light or some impurity. The comparison here with the problem of homolytic versus heterolytic reactions of halogens and hydrogen halides in organic chemistry is unmistakable.

Kochi's data include some measurements, albeit not strictly first-order and in the absence of air, on the decomposition of the benzylchromium ion in 0·1M-perchloric acid, and these can be used to derive an approximate stability order for the various penta-aquochromium ions at 28°. It is benzyl-(10^4) > 3-pyridiomethyl-(80) > 1-methyl-3-pydridiomethyl-(60) > 4-pyridiomethyl-(5) > 1-methyl-2-pyridio-methyl-(4) > 2-pyridiomethyl-(2).

The limitations of such a reactivity order in reactions of different activation energy is well demonstrated by a comparison of the rate of the uncatalysed and acetate catalysed reactions of the 4-pyridiomethylchromium ion; at 25° the former is some 10 times faster than the latter, but at 55° the two have almost the same rates.

The presence of added salts or acid also has an effect on the products of the reactions, but because of the limited accuracy of the product proportions and the uncertainty of the oxygen concentration in 5M- and 0·5M-perchloric acid, only a few conclusions can be drawn. The amount of methylpyridine formed in 0·5M- and 4·5M-perchloric acid is almost the same, giving support for the view that this is formed by a direct interaction between the forming pyridiomethyl radical and one of the water molecules co-ordinated to the chromous ion immediately after the transition state. On the other

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hand, the yields of pyridine-aldehyde and dipyridylethane are markedly different in the two solutions. The high yield of dipyridylethane in 4·5M-perchloric acid is unlikely to be a result solely of the reaction of the pyridiomethyl radical with the pyridiomethylchromium ion, and is almost certainly due partly to the dimerisation of the pyridiomethyl radical. This suggests that the pyridiomethyl radical must be very much more stable towards oxygen than the benzyl radical, and this may be associated with the corresponding stability of the pydridiomethyl chromium ion towards oxygen. In the more dilute acid solutions, the rate of formation of the pyridiomethylchromium ions is some 15 times slower than in strong acid, and the concentration of pyridiomethyl radicals present at any stage of the reaction will be correspondingly lower. Since the rate of dimerisation of these radicals is proportional to the square of their concentration, this means that the reaction with oxygen to form the pyridine-aldehyde will be much more favourable in dilute acid, as indeed observed.

EXPERIMENTAL

Materials.—Perchloric acid was Hopkin and Williams AR grade; lithium perchlorate was Hopkin and Williams Lab. reagent grade; and sodium acetate was B.D.H. hydrated AnalaR reagent. Purified solutions of penta-aquo-2-, -3-, and -4-pyridiomethylchromium(III) perchlorates and of penta-aquo-1-methyl-2-pyridiomethylchromium(III) perchlorate were prepared as described previously.[1] 3-*Bromomethyl*-1-*methylpyridinium bromide* was prepared by the method previously described for 2-bromomethyl-1-methylpyridinium bromide.[1] It had m. p. 166—168° (Found: C, 31·9; H, 3·4; Br, 59·5; N, 5·1. $C_6H_7Br_2N$ requires C, 31·5; H, 3·4; Br, 59·9; N, 5·2%). A solution of *penta-aquo*-1-*methyl*-3-*pyridiomethylchromium*-(III) *perchlorate* was prepared from 3-bromomethyl-1-methylpyridinium bromide by the general method described previously.[1] More concentrated solutions of the pyridiomethylchromium ions than previously described were made by eluting the ions from the ion-exchange resin with 2·5M-perchloric acid. In this way solutions of up to 0·074M-pyridiomethylchromium perchlorate were obtained.

Kinetics.—(a) A small quantity of a concentrated stock solution of the complex ion was added to a larger thermostatted quantity of perchloric acid such that the final concentration of complex was between 3×10^{-3} and 5×10^{-5}M and the final concentration of perchloric acid was between 5·5 and 2×10^{-3}M. In the case of the more rapid reactions, samples were taken at intervals and quenched in ice. The ultraviolet spectrum of each sample was then measured at the end of the reaction. In slower reactions the spectra of aliquots were measured directly. Rate coefficients were calculated by standard methods for first-order reactions from the changes in the optical density at one or more wavelengths. (b) In those runs where the concentration of complex ion was 2×10^{-2}M, the freshly mixed solution in the thermostat was below the desired temperature and the first sample was taken only when the desired temperature had been attained. In some cases oxygen was bubbled through these solutions; in others the reaction flask had a large dead-space and was shaken at frequent (*ca.* 1 min.) intervals in the thermostat. (c) In one run 0·5 ml. of the stock solution was added to 25 ml. D_2O rather than H_2O.

Products.—The solution of decomposed complex ions ($t >$ 10 half-lives) was made alkaline with sodium carbonate and extracted with 4 × 15 ml. portions of ether. The etheral solution was dried ($MgSO_4$) and evaporated to dryness at 50°. The products in the residue were identified as follows: 1,2-di-4′-pyridylethane as described in Part I; pyridine-4-aldehyde from its p.m.r. spectrum and the formation of a 2,4-dinitrophenylhydrazone; 4-methylpyridine from its p.m.r. spectrum. Product proportions were estimated from the p.m.r. spectra. Products of reaction of penta-aquo-2- and -3-pyridiomethylchromium(III) ion were isolated and characterised in a similar manner.

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William Ramsay and Ralph Forster Laboratories,
University College, Gower Street,
London W.C.1.

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