

Kinetics and Mechanism of the Acetate Assisted Cleavage of the Chromium–Carbon Bond of Hydroxymethylpenta-aquachromium(III)

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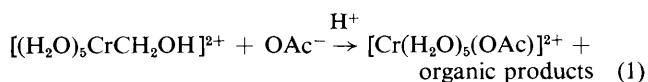
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Acetate ions greatly accelerate chromium–carbon bond cleavage in $[(\text{H}_2\text{O})_5\text{CrCH}_2\text{OH}]^{2+}$ to give $[\text{Cr}(\text{H}_2\text{O})_5(\text{OAc})]^{2+}$.

Mechanisms for the hydrolysis and spontaneous cleavage of the chromium(III)–carbon bond in organochromium(III) complexes in aqueous solution are quite well established.¹ However, the effects of added ions on the rates of Cr–C bond cleavage have not been investigated extensively, and the mechanism is not well understood.²

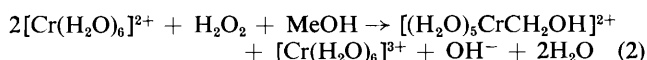
We have found that the rate of Cr–C bond cleavage in $[(\text{H}_2\text{O})_5\text{CrCH}_2\text{OH}]^{2+}$ is greatly accelerated in lithium acetate–acetic acid buffer solutions, resulting in the formation of $[\text{Cr}(\text{H}_2\text{O})_5(\text{OAc})]^{2+}$ ions. We report herein the kinetic results for this reaction and the mechanism deduced from the kinetic data.

The $[\text{Cr}(\text{H}_2\text{O})_5(\text{OAc})]^{2+}$ ions were separated from the reaction mixture on an SP-Sephadex C-25 (Na^+ form) cation exchange column, and were characterized by their u.v.–visible absorption spectrum.³ The yield of $[\text{Cr}(\text{H}_2\text{O})_5(\text{OAc})]^{2+}$ was in agreement with the stoichiometry of equation (1).



Kinetic measurements were made at ionic strength (I) 1.0 M (LiClO_4) and 25.0 °C under a nitrogen atmosphere. The $[(\text{H}_2\text{O})_5\text{CrCH}_2\text{OH}]^{2+}$ solutions were prepared from $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, H_2O_2 , and MeOH [equation (2)]⁴ immediately before the kinetic measurements. In our experiments, the concentration of H_2O_2 was controlled to be slightly in excess of

the stoichiometric amount in order to eliminate the unreacted Cr^{2+} ions in the $[(\text{H}_2\text{O})_5\text{CrCH}_2\text{OH}]^{2+}$ solution.



The kinetics of the reaction of $[(\text{H}_2\text{O})_5\text{CrCH}_2\text{OH}]^{2+}$ with acetate ions were studied by the use of a Union-Giken RA401 stopped-flow spectrophotometer under pseudo-first-order conditions; concentrations of acetate ions greatly exceeded those of the organochromium complex. The hydrogen ion concentrations were measured by a Toa HM-20B pH meter calibrated against standard HClO_4 solutions at $I = 1.0$ M (LiClO_4).

The reactions obeyed pseudo-first-order kinetics over at least three half-lives, and the pseudo-first-order rate constants, k_{obs} , were determined by the standard method; they were dependent on the concentration of both the hydrogen ions and the acetate ions as shown in Figure 1. The kinetic behaviour is compatible with the reaction scheme given by reactions (3)–(6), where K_{CrOAc} is the equilibrium constant of reaction (3), and k_a , k_b , and k_c are the rate constants for reactions (4), (5), and (6), respectively.

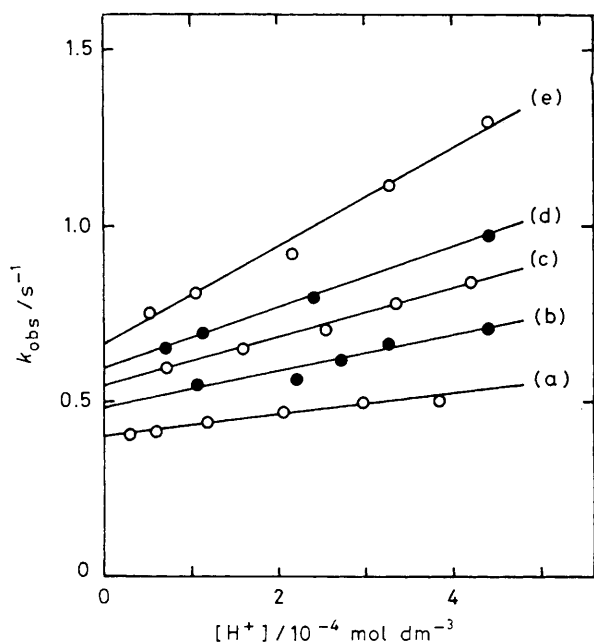
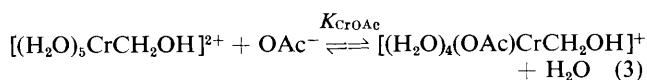


Figure 1. Relation between k_{obs} and $[\text{H}^+]$ for the reaction of $[(\text{H}_2\text{O})_5\text{CrCH}_2\text{OH}]^{2+}$ with acetate ions: $[\text{OAc}^-]/\text{dm}^3 \text{ mol}^{-1} = 0.0500$ (a), 0.0650 (b), 0.0800 (c), 0.100 (d), and 0.130 (e).

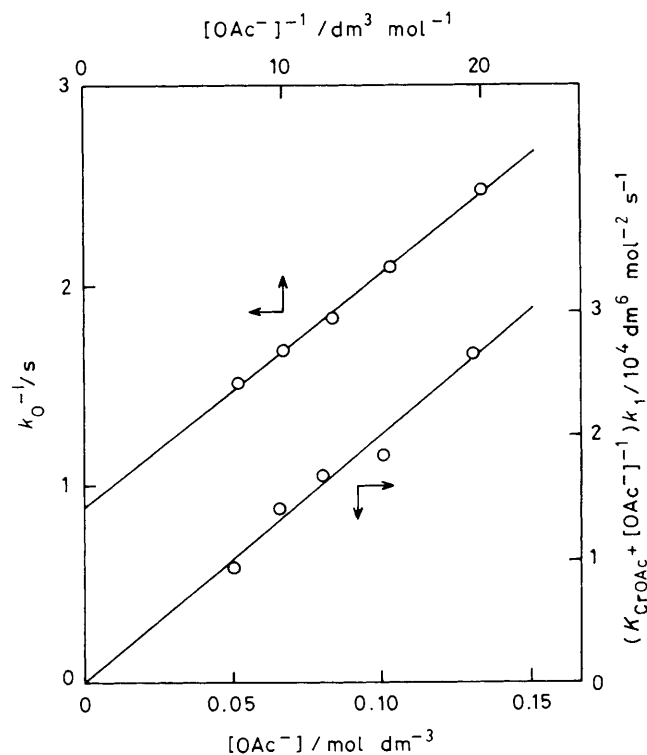
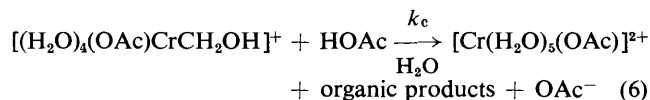
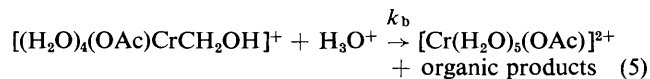
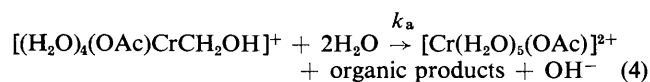


Figure 2. Plots of equation (8) (upper) and equation (9) (lower).



Reactions (3)–(6) give rate equation (7), where k_0 and k_1 are described by equations (8) and (9); K_{HOAc} is the acid dissociation constant of acetic acid. The equilibrium and rate constants in equations (8) and (9) were determined from the plots shown in Figure 2; $K_{\text{CrOAc}} = 11 \pm 1 \text{ dm}^3 \text{ mol}^{-1}$, $k_a = 1.12 \pm 0.07 \text{ s}^{-1}$, $k_b < 2 \times 10^2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, and $k_c = 0.6 \pm 0.2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

$$k_{\text{obs}} = k_0 + k_1 [\text{H}^+] \quad (7)$$

$$1/k_0 = 1/(k_a K_{\text{CrOAc}} [\text{OAc}^-]) + 1/k_a \quad (8)$$

$$(K_{\text{CrOAc}} + 1/[\text{OAc}^-])k_1 = k_c K_{\text{CrOAc}} [\text{OAc}^-]/K_{\text{HOAc}} + k_b K_{\text{CrOAc}} \quad (9)$$

The kinetic results show that the intermediate, $[(\text{H}_2\text{O})_4(\text{OAc})\text{CrCH}_2\text{OH}]^+$, undergoes much faster Cr–C bond cleavage than the penta-aqua species, $[(\text{H}_2\text{O})_5\text{CrCH}_2\text{OH}]^{2+}$;

reaction (4) is 1600 times faster than the hydrolysis of $[(\text{H}_2\text{O})_5\text{CrCH}_2\text{OH}]^{2+}$ ($7.0 \times 10^{-4} \text{ s}^{-1}$).⁴ Replacement of a co-ordinated water molecule by an acetate ion, which is more basic, will facilitate the elimination of the hydroxymethyl group.

The present work provides evidence that the accelerated cleavage of the Cr–C bond occurs *via* the ligation of the added anion. Some studies indicate that the position *trans* to the alkyl group in penta-aqua-alkylchromium(III) complexes is a labile substitution site.^{5–8} This suggests that the replacement of a water molecule in $[(\text{H}_2\text{O})_5\text{CrCH}_2\text{OH}]^{2+}$ by an acetate ion [reaction (3)] occurs at the position *trans* to the hydroxymethyl group.

The authors thank Drs. J. H. Espenson and A. Bakač for helpful discussions.

Received, 26th April 1983; Com. 516

References

- 1 J. H. Espenson, *Adv. Inorg. Bioinorg. Mech.*, 1982, **1**, 1.
- 2 J. K. Kochi and D. Buchanan, *J. Am. Chem. Soc.*, 1965, **87**, 853.
- 3 E. Deutsch and H. Taube, *Inorg. Chem.*, 1968, **7**, 1532.
- 4 W. Schmidt, J. H. Swinehart, and H. Taube, *J. Am. Chem. Soc.*, 1971, **93**, 1117.
- 5 S. K. Malik, W. Schmidt, and L. O. Spreer, *Inorg. Chem.*, 1974, **13**, 2986.
- 6 W. R. Bushey and J. H. Espenson, *Inorg. Chem.*, 1977, **16**, 2772.
- 7 J. Azram, H. Cohen, and D. Meyerstein, *J. Coord. Chem.*, 1977, **6**, 249.
- 8 A. Bakač, J. H. Espenson, and L. P. Miller, *Inorg. Chem.*, 1982, **21**, 1557.