Slow Dissociation of the Chromium(II) Acetate Dimer

By Roderick D. Cannon* and Jennifer S. Lund

(*School of Chemical Sciences, University of East Anglia, University Plain, Norwich* NOR 88C)

Summary Oxidation and substitution reactions of tetra-μ-acetato-dichromium(II) in aqueous medium are preceded by a unimolecular dissociation, the rate of which is consistent with a simple ligand-field model.

We have studied redox and substitution reactions of chromium(II) in aqueous acetate media [*e.g.* equations (1) and (2)] and have elucidated the role of the monomer–dimer equilibrium. Oxidations by $Cr(NH_3)_5Cl^{2+}$, $Cr(NH_3)_5Br^{2+}$, $Co(NH_3)_5OH^{2+}$, $Co(NH_3)_5(nta)H^+$ (where H_3nta = nitrilotriacetic acid), and $Co(edta)^-$ obey rate law (5) with

$$Cr(NH_3)_5Cl^{2+} + \tfrac{1}{2}Cr_2(OAc)_4 + 5\,HOAc \rightarrow \tfrac{1}{2}Cr_2(OAc)_4 + Cr(OAc)_2Cl + 5NH_4^+ + 5\,OAc^- \qquad (1)$$

$$H_2edta^{2-} + \tfrac{1}{2}Cr_2(OAc)_4 \rightarrow Cr(edta)^{2-} + 2HOAc \qquad (2)$$

various rate and activation parameters. Oxidations by $Co(C_2O_4)_3^{3-}$, $Co(NH_3)_5Cl^{2+}$, $Co(NH_3)_5Br^{2+}$, and I_2, and also replacement reactions involving multidentate ligands, obey rate law (6) all with very similar rate and activation parameters. Typical concentration ranges used were: oxidant or chelating agent 2—20 mM, chromium(II) 1—8 mM. Most reactions were carried out in buffer mixtures with [HOAc] = [OAc$^-$] = 0·5 M, but in the reactions with $Cr(NH_3)_5Cl^{2+}$, $Co(edta)^-$, and $Co(NH_3)_5Cl^{2+}$ it was established that rates were independent of both [HOAc] and [OAc$^-$] when these were varied separately over the range 0·2—1·0 M. At [OAc$^-$] $<$ 0·2 M dissociation of the dimer becomes extensive and other different rate laws come into play.[1]

All these observations are consistent with a common mechanism:†

$$Cr_2(OAc)_4 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} 2\,Cr(OAc)_2 \qquad (3)$$

$$Cr(OAc)_2 + X \xrightarrow{k_2^{X}} Products \qquad (4)$$

$$-\frac{d}{dt}[Cr_2(OAc)_4] = k_2^{X}(k_1/2k_{-1})^{\frac{1}{2}}[Cr_2(OAc)_4]^{\frac{1}{2}}[X] \qquad (5)$$

$$-\frac{d}{dt}[Cr_2(OAc)_4] = k_1[Cr_2(OAc)_4][X]^0 \qquad (6)$$

---

† The two water molecules in $Cr_2(OAc)_4,2H_2O$ are labile and easily replaced by other donor groups and it is probable that at the higher acetate concentrations used one or two acetate ions are attached. It makes no difference to any of the present arguments if the formulae $Cr_2(OAc)_4$, $Cr(OAc)_2$ *etc.* are replaced by $Cr_2(OAc)_6^{2-}$, $Cr(OAc)_3^-$ *etc.* The actual species denoted as dimer and monomer may in fact be equilibrium mixtures of these forms [*cf.* R. D. Cannon, *J. Chem. Soc.* (*A*), 1968, 1098].

Rate law (5) is obtained when reaction (4) is rate-determining, provided that the equilibrium (3) lies predominantly on the left-hand side; rate law (6) is obtained when reaction (4) is fast and the forward step of reaction (3) is rate-determining.

At lower chromium(II) concentrations we find deviations from rate law (5), consistent with a right-ward displacement of the equilibrium (3).

$$-\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{Cr(NH_3)_5Cl^{2+}}] = k_2[\mathrm{Cr(OAc)_2}][\mathrm{Cr(NH_3)_5Cl^{2+}}]$$

$$= \tfrac{1}{4}k_2K_1[\mathrm{Cr(NH_3)_5Cl^{2+}}][(1 + 8[\mathrm{Cr^{II}}]_{\mathrm{T}}K_1{}^{-1})^{\frac{1}{2}} - 1] \qquad (7)$$

where $k_2 = 0{\cdot}48\ \mathrm{M^{-1}\,s^{-1}}$, $K_1 = k_1/k_{-1} \approx 4 \times 10^{-4}\ \mathrm{M}$ at 25°. Data from all reactions obeying rate law (6) give $k_1 = 6{\cdot}0 \times 10^2\ \mathrm{s^{-1}}$, $\Delta H_1 = 15{\cdot}2$ kcal mol^{-1} whence $k_{-1} = 1{\cdot}5 \times 10^6\ \mathrm{M^{-1}\,s^{-1}}$. All values are for ionic strength 1·0 M ($\mathrm{NaClO_4}$).

We suggest that the rate-determining elementary step in reaction (3) is the breaking of a single chromium–oxygen bond. Simultaneous cleavage of two or more bonds is unlikely, and pre-equilibria involving complete separation of acetate ions are ruled out by the zero-order dependence on acetate ion. Compared with other ligand replacement reactions of chromium(II)‡ the value of k_1 is remarkably small, but it can be rationalised in terms of the electronic structure of the dimer. It is known[2] that all the 3d electrons are paired but is seems likely that the major contribution to metal–metal bonding is due to the d_{z^2} orbitals. If so, the spatial arrangement of the other three 3d electrons on each chromium atom is similar to that in a spin-free d^3 mononuclear complex, that is, $\mathrm{V^{2+}}$. Our values of k_1 and $\Delta H^{\ddagger}$ are indeed similar to those for replacement of water on $\mathrm{V^{2+}{\cdot}aq}$, namely 90 s^{-1}, ($\Delta H^{\ddagger} = 16{\cdot}4$ kcal mol^{-1}) for water exchange[3] and 70—120 s^{-1} ($\Delta H^{\ddagger} = 15{\cdot}3$ kcal mol^{-1}) for entry of $\mathrm{NCS^-}$ from the outer co-ordination sphere.[4]

This argument suggests the general prediction that where a binuclear complex involves strong σ-bonding the kinetic behaviour of the equatorial ligands will resemble that of ligands in mononuclear complexes of metals of the same valency, one place to the left in the Periodic Table. Thus we expect an analogy between $\mathrm{Rh_2(OAc)_4}$ and $\mathrm{Ru^{II}}$ in some appropriate complex; between $\mathrm{Re_2Cl_8^{2-}}$ and $\mathrm{WCl_6^{3-}}$; between $\mathrm{Mn_2(CO)_{10}}$ and $\mathrm{Cr(CO)_6}$; and so on. When the "appropriate complex" does not exist we may say instead that rates of replacement will be slower than in a corresponding mononuclear complex of the same metal ion, but faster than in the corresponding complex of the same metal with the next higher oxidation number. This is borne out in the case of the molybdenum(II) dimer: replacement of water in $\mathrm{Mo_2{}^{4+}{\cdot}aq}$ is slower than in $\mathrm{Mo^{2+}{\cdot}aq}$ but faster than in $\mathrm{Mo^{3+}{\cdot}aq}$.[7]

We thank the Royal Society (London) and the Science Research Council for grants towards the purchase of equipment. One of us (J.S.L.) holds an S.R.C. research studentship.

(*Received*, 20*th August* 1973; *Com.* 1201.)

---

‡ The specific rate for exchange of water molecules between $\mathrm{Cr^{2+}{\cdot}aq}$ and solvent exceeds $10^8\mathrm{s^{1-}}$ (*cf.* M. Eigen, *Ber. Bunsengesellschaft. Phys. Chem.*, 1963, **67**, 753).

[1] R. D. Cannon and J. S. Lund, to be published.
[2] C. Furlani, *Gazzetta*, 1957, **87**, 876.
[3] M. Olsen, Y. Kanazawa, and H. Taube, *J. Chem. Phys.*, 1969, **51**, 389.
[4] K. Kustin and J. Swinehart, *Progr. Inorg. Chem.*, 1970, **13**, 107, 141.
[5] H. Taube, personal communication.