Notes

Kinetics of Silver(II) Oxidation of Metal Cations

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The oxidation of Fe^{2+}, Mn^{2+}, Co^{2+}, Ce^{3+}, and VO^{2+} by silver(II) has been investigated with a stopped-flow technique. The reactions of Mn^{2+} and Ce^{3+} occur through two competitive paths involving Ag^{2+} and $AgOH^{+}$. For the other cations a single pathway with Ag^{2+} as oxidant has been observed. An inner-sphere interaction mechanism is proposed and discussed with reference to the electron configuration of the reductant and to the behaviour predicted by the Marcus cross relation.

The mechanisms of oxidations by Ag^{II} have been the subject of several investigations in which organic [1] and inorganic [2] substrates have been used. The Ag^{II}/Ag^{I} couple has a very high reduction potential (*ca.* 2 V in 1.0 mol dm^{-3} $HClO_4$ [3]) and Ag^{II} reacts rapidly even with substrates that exhibit sluggish behaviour towards other commonly employed oxidants.

We report here the oxidation of a series of metal ions (Fe^{II}, Mn^{II}, Co^{II}, Ce^{III}, and V^{IV}) which show a wide range of reduction potentials and of intrinsic self-exchange rates. The rates of oxidation of a similar series of metal ions by Ag^{II} have been previously reported.[4] The present investigation involves a study of the acid dependence of these reactions and thus leads to values of rate constants for specific reaction steps.

Calculations in which these values are used together with values of overall equilibrium constants and self-exchange rate constants throw some light on the question of the occurrence of outer-sphere or inner-sphere mechanisms.

Experimental

Materials.—Cobalt(II), manganese(II), and cerium(III) perchlorates were obtained from the corresponding carbonates and perchloric acid; the solids were recrystallized twice from water. Iron(II) perchlorate solutions were obtained by dissolving pure iron wire in a known excess of perchloric acid. Vanadium(IV) perchlorate was obtained by mixing equivalent volumes of Ba perchlorate ($BaCO_3 + HClO_4$) and V^{IV} sulphate solutions; precipitated $BaSO_4$ was then removed by filtration on a MF Millipore membrane (pores 0.45 µm). Silver(I) perchlorate solutions were obtained by dissolving Ag_2O in a known excess of $HClO_4$; Ag^{II} perchlorate solutions were obtained by anodic oxidation as previously described.[5]

Procedure.—Experiments were performed on a Durrum Stopped-flow apparatus (model D 110). All reactions were investigated at 25.0 °C under pseudo-first-order conditions {excess of reductant: $[Mn^{II}] = (3—6) \times 10^{-4}$, $[Co^{II}] = (1—5) \times 10^{-3}$; $[Ce^{III}] = (3 \times 9) \times 10^{-4}$, $[V^{IV}] = (1—5) \times 10^{-3}$, $[Ag^{II}] = (0.4—2.0) \times 10^{-4}$ mol dm^{-3}} with the exception of Fe^{II} whose reaction was followed under second-order conditions {$[Ag^{II}] \simeq [Fe^{II}] = (1—3) \times 10^{-4}$ mol dm^{-3}}. The reactions were followed at 470 nm, where Ag^{II} is the only absorbing species, at different acidities ($[HClO_4] = 1.0—4.0$ mol dm^{-3}) and at constant ionic strength $I = 4.0$ mol dm^{-3} ($NaClO_4$ was used; preliminary runs, carried out with $LiClO_4$ gave identical results). Excess Ag^{I} (0.10 mol dm^{-3}) was present in order to prevent Ag^{II} disproportionation.

Table 1. Second-order rate constants (k_{II}/dm^3 mol^{-1} s^{-1}) for the oxidation of metal cations by Ag^{II} at 25.0 °C and at different acidities

		[HClO$_4$]/mol dm^{-3}				
Metal		1.00	1.50	2.00	3.00	4.00
Fe^{II}	$10^{-5}k_{II}$	1.3	1.4	1.5	1.5	1.5
Co^{II}	$10^{-3}k_{II}$	2.4	2.7	2.7	2.4	2.2
Ce^{III}	$10^{-3}k_{II}$	3.2	2.8	2.5	1.8	1.4
Mn^{II}	$10^{-4}k_{II}$	7.5	6.0	5.3	4.2	2.9
V^{IV}	$10^{-3}k_{II}$	3.8	3.8	3.7	3.9	3.9_5

Results and Discussion

A single one-electron oxidation according to the stoicheiometry of equation (1) was assumed (M = metal). The

$$Ag^{II} + M^{n+} \longrightarrow Ag^{I} + M^{(n+1)+} \qquad (1)$$

appropriate first-order and second-order plots were linear in accordance with the rate equation (2). Values of the second-

$$-d[Ag_{II}]/dt = k^{II}[M^{n+}][Ag^{II}] \qquad (2)$$

order rate constants (k_{II}) are given in Table 1. The values at 4.0 mol dm^{-3} $HClO_4$ are in good agreement with those reported earlier.[4] These results are consistent with the occurrence of the following rate-determining steps (3) and (4), from which

$$Ag^{2+} + M^{n+} \xrightarrow{k_1} Ag^{+} + M^{(n+1)+} \qquad (3)$$

$$AgOH^{+} + M^{n+} \xrightarrow{k_2} Ag^{+} + M^{(n+1)+} + OH^{-} \qquad (4)$$

follows equation (5) where K_h is the hydrolysis equilibrium constant for the formation of $AgOH^+$ from Ag^{2+}.

$$k_{II} = (k_1 + k_2K_h[H^+]^{-1})/(1 + K_h[H^+]^{-1}) \qquad (5)$$

Plots of $k_{II}(1 + K_h[H^+]^{-1})$ (assuming that $K_h = 0.40$ mol dm^{-3} at 25.0 °C) [1a] as a function of $[H^+]^{-1}$ gave the values of k_1 and k_2K_h reported in Table 2. Both pathways are present for Mn^{II} and Ce^{III}, while for Fe^{II}, Co^{II}, and V^{IV}, reaction (2) with the unhydrolysed species is the only active pathway. Participation of the $MOH^{(n-1)+}$ cation as responsible for the inverse acid dependence has been discarded as a possibility since this would lead to k_2 values exceeding 10^9 dm^3 mol^{-1} s^{-1}

Table 2. Values of k_1 and k_2K_h [equations (3)—(5)] for the oxidation of the investigated metal cations by Ag^{II} at 25.0 °C

	Fe^{II}	Co^{II}	Ce^{III}	Mn^{II}	V^{IV}
$k_1/dm^3\ mol^{-1}\ s^{-1}$	1.4×10^5	2.4×10^3	7.5×10^2	1.0×10^4	3.9×10^3
k_2K_h/s^{-1}	—	—	4.0×10^3	8.0×10^4	—

Table 3. Experimental and computed parameters (see text) for the investigated reactions

Metal cation	E^0/V	K_{eq}	$k_{22}/$ $dm^3\ mol^{-1}\ s^{-1}$	k_{12} (exp.)/ $dm^3\ mol^{-1}\ s^{-1}$	f	$k_{11}/dm^3\ mol^{-1}\ s^{-1}$
Fe^{II}	0.77	6.2×10^{20}	4.0	1.4×10^5	1.7×10^{-4}	4.6×10^{-8}
Co^{II}	1.84	5.1×10^2	3.3	2.4×10^3	0.79	4.3×10^3
Ce^{III}	1.61	3.9×10^6	4.4	7.5×10^2	0.33	0.10
Mn^{II}	1.51	1.9×10^8	2×10^{-4}	1.0×10^4	0.16	1.7×10^4

(*i.e.* exceeding the diffusion limit for $2+/n+$ like-charged reactants in a 4.0 mol dm^{-3} ionic medium).

The derived parameters allow two distinct observations to be made regarding the $AgOH^+$ and Ag^{2+} active pathways. First, the reactivity of $AgOH^+$ may be interpreted in terms either of an inner-sphere mechanism through a hydroxo-bridge activated complex, or of a hydrogen atom transfer in a hydrogen-bonded outer-sphere mechanism.[6] The absence of such a path for Fe and Co suggests that a specific inner-sphere interaction is operating. If the electron configurations of M^{n+} and $M^{(n+1)+}$ are considered it seems that for Mn^{II} and Ce^{III} an electron is abstracted from an orbital which points along one co-ordination position for a six-co-ordinated system: from an e_g orbital for $Mn^{II} \longrightarrow Mn^{III}$ ($t_{2g}^3e_{2g}^2 \longrightarrow t_{2g}^3e_g^1$), and for $Ce^{III} \longrightarrow Ce^{IV}$ from an f orbital whose electron density again is distributed along axes of octahedral symmetry.[7] In these cases OH^- bridging gives a specific inner-sphere interaction along one octahedral direction making easier the electron transfer.[8] The bridging role of OH^- in the case of the Ce^{III}/Ag^{II} and Mn^{II}/Ag^{II} reactions may also be considered in the light of the high tendency to hydrolyse of the Ce^{IV} and Mn^{III} species whose configurations are forming in the activated state. For Fe^{II}, the absence of pathway (4) may well be ascribed to the electron abstraction from a (non-bonding) t_{2g} orbital ($Fe^{II} \longrightarrow Fe^{III}$: $t_{2g}^4e_g^2 \longrightarrow t_{2g}^3e_g^2$) and, for V^{IV} and Co^{II} reorganizations in the co-ordination sphere are involved which may be hindered by the presence of an OH^- bridge. [In the case of V^{IV} these are associated with the inter-conversion of oxo- and hydroxo-species, and in the case of Co^{II}, although (as for Mn^{II} and Ce^{III}) an electron is transferred from an e_g orbital ($t_{2g}^5e_g^2 \longrightarrow t_{2g}^6e_g^0$), the remaining e_g electron then passes to the t_{2g} level, a process that would involve not only a spin change but some reorganization of the co-ordination sphere resulting from the change in the number of bonding electrons.]

Turning now to the reaction of the Ag^{2+} ion, the electron exchange may take place through a simple outer-sphere electron transfer or through an activated complex where some specific interactions between reactant orbitals occur. In the first case the rates may be predicted by the Marcus cross relation[9] [equations (6) and (7)], where equation (8) applies

$$Ox_1 + Red_2 \xrightarrow{k_{12}} Red_1 + Ox_2 \qquad (6)$$

$$k_{12} = (k_{11}k_{22}K_{12}f)^{\frac{1}{2}} \qquad (7)$$

$$\log f = (\log K_{12})^2/[4 \log (k_{11}k_{22}/Z^2)] \qquad (8)$$

and k_{11} and k_{22} are the self-exchange rate constants for the single redox couples in equation (6), K_{12} is the equilibrium quotient of equation (6) and Z is the collision frequency ($Z = 10^{11}\ s^{-1}$).

In order to test the occurrence of a purely outer-sphere electron transfer the applicability of equation (7) to the present systems may be considered. With the knowledge of experimental k_{12} values, and with the available E^0 and k_{22} values for each oxidized cation, it is possible to obtain [with an iteration procedure to account for the f factor in equation (7)] the self-exchange rate k_{11} for the Ag^{II}/Ag^{I} couple. Table 3 reports the experimental and other available data together with the computed k_{11} values [the V^{IV} rate has not been included since atom transfer to yield $VO_2(OH)$ species from VO^{2+} make equation (7) inapplicable].

As can be seen, values ranging from 10^{-8} to 10^4 are obtained. thus suggesting that equation (7) is not valid and that a simple outer-sphere electron transfer does not apply for these Ag^{II} oxidation reactions. In fact these discrepancies are much higher than those observed[10] for other outer-sphere reactions where k(exp.) > k(computed) for $\Delta G^{\ominus} \ll 0$ (*e.g.* for Fe^{II} oxidation). Moreover, the change of spin multiplicity for the Co^{II}/Co^{III} oxidation should be accounted for in equation (6), by a 10^{-6} factor[11] which would not lead to better agreement in the k_{11} values reported in Table 3.

Several possible reasons may be considered for the above discrepancies: (*i*) non-adiabaticity for the electron-transfer act [this would break down one condition for the validity of equation (7)]; (*ii*) changes in spin multiplicity for one or both reacting partners; (*iii*) strong orbital interactions between the reactants. Possibly (*ii*) is relevant for the Co^{II} reactions but no clear reasons are apparent in the other cases. The work to bring reactants and products together in the activated state is expected to be low at the investigated ionic strength and should be nearly cancelled, so that seems irrelevant in comparison to the observed discrepancies.

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