ELSEVIER

Inorganica Chimica Acta 225 (1994) 83–88

Inorganica Chimica Acta

Electron transfer
122. Reductions of an N_4-coordinated complex of silver(III)

Sanchita P. Ghosh, Manik C. Ghosh, E.S. Gould*

Department of Chemistry, Kent State University, Kent, OH 44242, USA

Received 16 February 1994

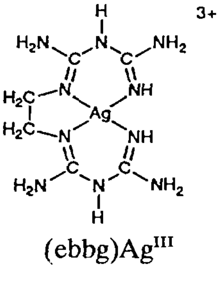
Abstract

The silver(III) complex of ethylenebis(biguanide), (ebbg)Ag^{III}, which is stable in aqueous acid, reacts readily with 2 equiv. each of V^{2+}, Cr^{2+}, Eu^{2+}, Fe^{2+} and $Ru(NH_3)_6{}^{2+}$ yielding Ag^+. Slower reactions with Ti(III) and $Fe(Me_2phen)_3{}^{2+}$ consume only 1 equiv. of these reductants but again yield Ag^+. The $2e^-$ reductants H_3AsO_3 and $HSO_3{}^-$ do not react. No Ag(II) species is detected in these reactions, either as a product or as a transient. At low reductant concentrations, reactions are first order in both redox partners, but at high [Fe^{2+}], there is evidence for partial formation of a 1:1 (ebbg)Ag^{III}–Fe^{II} complex ($Q_{assn} = 10\ M^{-1}$). Rates appear to be determined by the initial $1e^-$ reduction of (ebbg)Ag^{III} to its Ag^{II} analog, after which the latter is rapidly converted to Ag(I), either by a second reductant molecule or, in the case of the slower reductants, internal electron transfer with oxidation of the ligand. The latter process provides substantial driving force for it allows complete conversion to Ag(I) by several reductants having much more positive $E°$ values than that reported for (ebbg)$Ag^{III/II}$ (0.32 V). Kinetic selectivity patterns are consistent with the predominance of an outer-sphere path for all metal-center reductants examined. Specific rates for these reductions, in conjunction with the treatment of Marcus, led to a self-exchange rate $10^{5.8\pm0.8}$ $M^{-1}\ s^{-1}$ for this $Ag^{III/II}$ couple. The latter value is comparable to rates recorded for a number of 4d- and 5d-based systems, is considerably greater than many of those for 3d-based couples, and lies close to that for $Ag^{III/II}$ when both states are porphyrin-bound. The present results support the view that reductions of Ag(III) to Ag(I) in this system take place most easily by successive $1e^-$ steps, rather than by single $2e^-$ transactions. These $2e^-$ reductants that react most readily (e.g. ascorbic acid and H_2O_2) are those which can be oxidized in single electron steps. Reductions by formic acid and by primary alcohols, which may instead involve hydride transfer to Ag(III) are found to proceed much more sluggishly.

Keywords: Electron transfer; Kinetics and mechanism; Silver complexes; Polydentate ligand complexes; Chelate complexes

1. Introduction

Investigations of the redox reactions of tripositive silver [1] have been, in part, circumscribed by the instability of this state in the absence of base. A notable exception is the Ag(III) complex of ethylenebis(biguanide), (ebbg)Ag^{III}, salts of which are water soluble and stable for extended periods in strong aqueous acid. Despite a recent flurry of experimental activity treating oxidations by this unusual complex [2], no estimate for the electron self-exchange rate for the system (ebbg)$Ag^{III,\,II}$ has as yet been documented. The present contribution deals with reactions of this hypervalent silver species with metal-centered reductants.



(ebbg)Ag^{III}

2. Experimental

2.1. Materials

Ethylenebis(biguanide)silver(III) [(cbbg)Ag^{III}) derivatives were prepared by slight modifications of the method of Ray and Chakravarty [3a]. The copper(II) complex of this ligand was first prepared and then

---

*Corresponding author.

SSDI 0020-1693(94)04033-R

converted to the metal-free ligand hydrosulfate as described in Ref. [3b]. The very sluggish crystallization of the latter salt from its aqueous solution (requiring over 2 days at 0 °C) could be hastened by dilution with ethanol without affecting its purity; m.p. 262 °C (reported [3b] 263.5). The ligand hydrosulfate was converted to the sulfate of its Ag(III) complex by treatment with aqueous silver sulfate and potassium peroxydisulfate at 4 °C as described in Ref. [3b]. After 48 h at 0 °C, the red complex salt was filtered off and converted to the complex hydroxide by treatment with aqueous NaOH [3b]. The latter was then converted to the desired complex Ag(III) perchlorate by dissolving in a minimum volume of 0.01 M $HClO_4$, cooling, and then adding an equal volume of conc. $HClO_4$; $\epsilon_{380}^{\max} = 1190$ M^{-1} cm^{-1} (reported [2c] 1175).

Solutions of Fe^{2+} [4], Eu^{2+} [5], V^{2+} [6], Cr^{2+} [7] and $Mo_2O_4^{2+}$ [8] were prepared as perchlorates by literature methods, as were Ti(III) (tosylate) [9] and $Ru(NH_3)_6^{2+}$ (triflate) [10]. Solutions of $NaClO_4$, used as a supporting electrolyte in kinetic experiments, were prepared by reaction of $NaHCO_3$ with $HClO_4$. Iron(II) complexes of the type $Fe(lig)_3^{2+}$, derived from substituted 2,2′-bipyridines or 1,10-phenanthrolines were obtained as perchlorates from G.F. Smith Co. and were used as received, or were prepared as bis(perchlorates) from the respective ligands as described in Ref. [10].

2.2. *Stoichiometric experiments*

Stoichiometries of reductions of $(ebbg)Ag^{III}$ in aqueous acid were, in most cases, measured at 380 nm by adding deficient quantities of the reductant to a known excess of Ag(III). The resulting decreases in absorbance were compared to those observed with a slight excess of reductant. The reaction with Fe^{2+} (aq.) was carried out with a known excess of reductant, after which a large excess (0.20 M) of NH_4SCN was added and Fe(III) was estimated as $FeNCS^{2+}$ ($\epsilon_{480} = 6.3 \times 10^3$ M^{-1} cm^{-1}). Stoichiometries of the reductions by $Mo_2O_4^{2+}$ and by $Fe(Me_2phen)_3^{2+}$ were estimated by spectrophotometric titration at 384 and 420 nm. Results are summarized in Table 1.

2.3. *Kinetic experiments*

Reactions were followed by measuring absorbance changes, employing either a Durrum-Gibson stopped-flow spectrophotometer equipped with an OLIS data acquisition system or a Beckman model 5260 recording spectrophotometer. All runs were carried out under N_2, and ionic strength was customarily maintained at 1.0 M by addition of $HClO_4/NaClO_4$. In most cases concentrations were adjusted so that less than 10% of the reagent in excess was consumed during the collection of data. Reactions generally yielded pseudo-first-order kinetic curves and were followed for at least 4 half-lives, and rate constants were evaluated by non-linear least-squares fittings to the relationship describing first-order decay. Specific rates greater than 50 s^{-1} were adjusted upward to accommodate the mixing rate associated with our stopped-flow instrument as described by Dickson and Margerum [11]. Rate constants for replicate runs diverged by less than 6%. Profiles associated with reductions by $(Me_2phen)_3Fe^{2+}$ exhibited slight distortion reflecting the slow decomposition of the unreacted reductant. Since this distortion was most pronounced near the end of each run, the rate constant for the primary reaction in this instance was estimated from initial slopes. The value so obtained is considered to be reliable to no better than 20%.

2.4. *Additional observations*

At 25 °C, $(ebbg)Ag^{III}$ reacts immeasurably slowly with the $2e^-$ reductants H_3AsO_3 and HSO_3^-, and with finely divided silver metal (prepared by treatment of $AgClO_4$ with $Eu(ClO_4)_2$). In contrast, the reaction with Cu^+ is too rapid to follow by conventional mixing. Reactions with the Fe(II) chelates of 2,2′-bipyridine and 1,10-phenanthroline, and with their ring-methylated analogs, were very nearly complete under our conditions, but the 5-nitro complex, $Fe(nitrophen)_3^{2+}$, did not react appreciably. Reactions with U(IV) and $Mo_2O_4^{2+}$ appeared to be autocatalytic, but the resulting decay profiles could not be deconvoluted meaningfully.

Solutions resulting from the reduction of $(ebbg)Ag^{III}$ (1×10^3 M) with Ti^{III} (5×10^{-4} M) in 1.0 M $HClO_4$ were examined by ESR spectroscopy but exhibited no absorbances attributable to monomeric Ag(II) species, even at 140 K.

3. Results and discussion

Reactions of the Ag(III) oxidant with 5 of the 8 metal center reductants examined are seen (Table 1) to exhibit stoichiometries approaching 2:1, indicating that $2e^-$ are transferred cleanly to Ag(III) in each of these cases, even when the reductant is very much in deficiency:

$$Ag^{III} + 2M^{II} \longrightarrow Ag^{I} + 2M^{III} \tag{1}$$

With the less powerful (and slower) donors, Ti(III), $Mo_2O_4^{2+}$ and $Fe(Me_2phen)_2^{2+}$ very nearly 1.0 reducing equiv. arises from each unit of added reductant. In such instances, however, neither electronic nor ESR spectra of the resulting solutions point to formation of a significant yield of an Ag(II) species. The picture is consistent with the intervention of an $(ebbg)Ag^{II}$ intermediate in each of these transformations. With the more rapid reductants, this transient is then reduced

Table 1
Stoichiometries of the reductions of ethylenebis(guanide)silver(III) [(ebbg)Ag^{III}]^{a}

Reductant (red.)	10^4[ox.] (M)	10^4[red.] (M)	Waiting period (min)	Δ[red.]/Δ[ox.]
V(II)	3.7	1.0–4.0	1.0–5.0	1.95 ± 0.07
Cr(II)	3.7	1.0–3.0	1.0–5.0	2.01 ± 0.12
$Ru(NH_3)_6^{2+}$ ^{b}	12.0	3.6–18.0	0.5	1.82 ± 0.02
Eu(II)	7.2	0.5–2.0	0.5	1.88 ± 0.04
Ti(III)	6.5–7.3	0.5–6.0	2.0–3.0	1.05 ± 0.04
$Fe(II)_{aq}$ ^{c}	0.5–1.0	100	5.0	1.96 ± 0.12
$Mo_2O_4^{2+}$			1.5–36.0	0.49^{d}
$Fe(Me_2phen)_3^{2+}$			9.0	1.02^{e}

[a] Reactions of 25 °C in 1.0 M $HClO_4$ unless otherwise indicated.
[b] Reactions in 1 M triflic acid.
[c] Stoichiometry obtained by measuring Fe(III) formed; $[H^+]=0.1$ M (see Section 2).
[d] Spectrophotometric titration at 384 nm.
[e] Spectrophotometric titration at 420 nm.

to Ag(I), but with the more sluggish reagents it instead undergoes internal redox with consumption of the ligand and formation of Ag(I), a step for which Banerjee and Banerjea [12] have presented independent evidence. As expected, the latter decomposition competes less favorably when the reductant is in large excess, as demonstrated by the approach to 2:1 stoichiometry observed here with Fe(II) (aq.).

Representative kinetic data, pertaining to reductions by Fe^{2+} (aq.) and V^{2+} (aq.), appear in Table 2. Rates with both reductants are seen to be very nearly independent of acidity within the range 0.1–1.0 M H^+, and reactions with Fe(II) exhibit signs of kinetic saturation at high [red.], indicating the formation of a weakly associated complex between redox partners. Data for the Ag(III)–Fe(II) system conform to rate law (2):

$$-\mathrm{d}[\mathrm{Ag(III)}]\mathrm{d}t=[\mathrm{Ag(III)}][\mathrm{Fe(II)}]\frac{k_{\mathrm{lim}}Q}{1+Q[\mathrm{Fe(II)}]} \qquad (2)$$

Table 2
Representative kinetic data for the reductions of ethylenebis(biguanide)silver(III) by Fe(II) and V(II)^{a}

Reductions by Fe(II)^{b}			Reductions by V(II)^{c}		
[red.] (mM)	$[H^+]$ (M)	10^3k^{d} (s^{-1})	$[Ag^{III}]$ (mM)	$[H^+]$ (M)	$10^{-2}k$ (s^{-1})
5.0	0.10	3.0 (3.2)	0.250	1.00	2.8
10.0	0.10	6.5 (6.1)	0.200	1.00	2.20
20.0	0.10	11.8 (11.3)	0.150	1.00	1.76
35.0	0.10	17.8 (17.6)	0.100	1.00	1.02
50.0	0.10	22 (23)	0.100	0.75	0.97
75.0	0.10	29 (29)	0.100	0.55	1.02
20.0	1.00	9.5 (11.3)	0.100	0.30	1.08
20.0	0.025	12.3 (11.3)	0.100	0.15	1.06

[a] $\mu=1.00$ M ($NaClO_4/HClO_4$); $\lambda=380$ nm.
[b] Reactions at 25.0 °C; $[Ag^{III}]=2.2\times10^{-4}$ M throughout.
[c] Reactions at 20.0 °C; $[V^{II}]=4.0\times10^{-5}$ M throughout.
[d] Pseudo-first-order rate constants; parenthetical values were calculated using rate law (2) in text and taking K as 9.5 M^{-1} and k_{lim} as 0.070 s^{-1}.

Refinement of observed rate constants yields an association quotient, Q, $=9.5\pm1.4$ M^{-1} and a limiting specific rate (at high $[Fe^{2+}]$) $=0.070\pm0.010$ s^{-1} (25 °C). No sign of such saturation is seen with the remaining reductants which were, however, employed at much lower concentrations. At low $[Fe^{2+}]$, reductions are very nearly first order in both redox components with a bimolecular rate constant of 0.67 M^{-1} s^{-1}.

Table 3 lists rate constants for reactions of (ebbg)Ag^{III} with additional metal-center reductants. The ease with which these conversions occur, in contrast to lack of reactivity of the 2e reagents, H_3AsO_3 and HSO_3^-, emphasizes the principal conclusion of this study – that for reduction of the Ag(III) complex at hand to Ag(I) (a net 2 unit change), pairs of single-electron transactions are greatly favored over single 2e processes. Profiles of these reductions show no irregularities attributable to the accumulation of the Ag(II) intermediate. We thus may infer that in each case, the rate is determined by the initial conversion to Ag(II) (reaction (3)) and that the subsequent consumption of this odd-electron state, either by additional reductant (4) or by internal decomposition (5) is rapid and, hence, kinetically silent.

$$(\mathrm{ebbg})\mathrm{Ag^{III}}+\mathrm{M^{II}}\longrightarrow(\mathrm{ebbg})\mathrm{Ag^{II}}+\mathrm{M^{III}}\quad(\text{slow})\qquad(3)$$

$$(\mathrm{ebbg})\mathrm{Ag^{II}}+\mathrm{M^{II}}\xrightarrow{\mathrm{H^+}}\mathrm{Ag^{I}}+\mathrm{M^{III}}+\mathrm{ebbgH^+}\quad(\text{rapid})\qquad(4)$$

$$(\mathrm{ebbg})\mathrm{Ag^{II}}\longrightarrow\mathrm{Ag^{I}}+\text{ligand oxidation products}\quad(\text{rapid})\qquad(5)$$

(with Ti^{III}, $Mo_2O_4^{2+}$ and $Fe(Me_2phen)_3^{2+}$)

Table 3
Rate constants for reactions of ethylenebis(biguanide)silver(III) with metal-center reductants[a]

Reductant (mM)	$[Ag^{III}]$ (mM)	$[H^+]$ (M)	Medium	k ($M^{-1}\ s^{-1}$)
Fe^{2+}(aq.) (5–75)	0.22	0.025–1.0	ClO_4^-	0.67[b]
V^{2+} (0.040)	0.10–0.25	0.15–1.0	ClO_4^-	$(1.07\pm0.05)\times10^6$
Eu^{2+} (0.040)	0.10–0.25	0.50–1.0	ClO_4^-	$(3.4\pm0.2)\times10^5$
Ti^{III} (0.060)	0.30–1.20	1.0[c]	$TosO^-$	50 ± 2
$Ru(NH_3)_6^{2+}$ (0.02–0.05)	0.035–0.050	0.5	Triflate	$(1.5\pm0.1)\times10^7$
Cr^{2+} (0.050)	0.050	1.0	ClO_4^-	$>5\times10^7$
Cu^+ (1.0)	1.60	1.0	ClO_4^-	$>6\times10^2$[d]
$Fe(Me_2phen)_3^{2+}$ (0.1–0.9)	0.013	0.11	ClO_4^-	4×10^2[e]

[a] Reactions were carried out at 20.5±0.5 °C; $\mu=1.0$ M, unless otherwise indicated.
[b] Limiting specific rate (25 °C) at low [red.]; at higher $[Fe^{II}]$, reactions followed Eq. (2) in text.
[c] Reactions at lower $[H^+]$ were complicated by precipitation.
[d] Reaction monitored by conventional mixing; Cu^+ solutions underwent rapid disproportionation to Cu metal and Cu^{2+} on contact with steel valve parts of stopped-flow system.
[e] Chelate of 5,6-dimethylphenanthroline. Specific rate ($\mu=0.11$ M) was calculated from initial slopes (see Section 2).

Accordingly, the rate constant for the initial electron transfer from V^{2+}, Eu^{2+}, Cr^{2+} or $Ru(NH_3)_6^{2+}$ may be taken as half that observed for the loss of $(ebbg)Ag^{III}$.

Although Banerjee and Banerjea [12] have described experiments confirming the destruction of the ligand, its oxidation products were not identified. Nevertheless, it is clear that step (5) provides a substantial measure of the overall driving force for the conversion to Ag(I) by the less powerful oxidants. This is especially so for the tris(chelates) of Fe(II) derived from substituted phenanthrolines and 2,2′-bipyridines. The latter reductants, having $E°$ values in the range 0.90–1.10 V [13], are found here to be oxidized readily although the formal potential for $(ebbg)Ag^{III/II}$, which pertains to the initial step, is recorded to be a much less positive value, 0.32 V (0.05 V versus SCE [14].

The substitution-inert character of the low-spin Ru(II) center dictates outer-sphere reduction by $Ru(NH_3)_6^{2+}$, and a similar conclusion applies to reduction by V^{2+}, which proceeds at a rate far above the limit (near 100 $M^{-1}\ s^{-1}$) for inner-sphere reductions imposed by slow substitution on this center [15]. Moreover, the rate ratio observed here, $k_V/k_{Eu}=3/1$, corresponds to that found by these 2+ reductants for bona fide outer-sphere cases [16]. We have employed data from the more rapid reductions, in the framework of the model of Marcus [17], to estimate a self-exchange rate for the couple $(ebbg)Ag^{III/II}$. In consideration of the range of ΔG_0 values within this series, we have used Eq. (6) [18], in which the rate constant, k_{12}, of an outer-sphere reaction is taken as the sum of three terms

$$\ln k_{12}=1/2\left[\ln(k_{11}k_{22}K_{12}) + \frac{[\ln K_{12}+(w_{12}-w_{21})/RT]^2}{4\left[\ln\frac{k_{11}/k_{22}}{Z^2}+\frac{(w_{11}+w_{22})}{RT}\right]}\right] + \frac{w_{11}+w_{22}-w_{12}-w_{21}}{2RT} \qquad (6)$$

where k_{11} and k_{22} are self-exchange rates for the oxidant and reductant, K_{12} is the equilibrium constant for the redox reaction, Z is the collision frequency, $10^{11}\ M^{-1}\ s^{-1}$, and the w terms are electrostatic work contributions from the reactants, the products, and the two self-exchanging systems. Each w term is, in turn, calculated by Eq. (7)

$$w_{cd}=4.23z_cz_d/a_{cd}(1+0.33a_{cd}\mu^{1/2}) \qquad (7)$$

where z terms are the ionic charges on interacting species c and d, μ is the ionic strength of the medium, and a_{cd} is the distance of closest approach, as estimated from the presumed geometry of the encounter and reported atomic and ionic radii.

Estimated terms contributing to the reduction of $(ebbg)Ag^{III}$ are listed in Table 4. Experimental values of the observed rate constants[1], k_{12}, in combination

---

[1] Because of problems resulting from precipitation at lower acidities, reductions by Ti(III) were examined only in 1.0 M H^+. The entry in Table 4 assumes the active reducing species to be $Ti(H_2O)_6^{3+}$. A number of reductions by Ti(III) are known to proceed principally through $Ti(OH)^{2+}$ [19]. Analogous treatment using $E°$ (≥ -0.080 V) and log k_{22} (-2.0) associated with the latter [19], in conjunction with a pK_a value of 2.0, yields log $k_{11}\geq3.5$ for $(ebbg)Ag^{III/II}$.

Table 4
Calculated self-exchange rates and contributing parameters for the reductions of ethylenebis(biguanide)silver(III)[a] (22 °C, $\mu = 1.0$ M)

Reductant	E°_{red} (V)	Log k_{22}[b]	Log K_{12}[c]	Log w_{12}[d]	Log f_{12}[e]	Log k_{12}	Log k_{11}[f]	Ref.
Fe^{2+}(aq.)	0.74	0.04	−7.16	0.018	−1.01	−0.49	7.1	[20,21]
Eu^{2+}	−0.38	−4.5	11.89	0.048	−1.81	5.3	4.9	[20,22]
V^{2+}	−0.26	−2.0	9.77	0.004	−1.40	5.7	5.0	[20,22]
$Ru(NH_3)_6^{2+}$	−0.067	3.6	4.30	0.074	−0.47	6.9	6.2	[23,24]
Cu^+	0.15	−5.0	2.90	0.148	−0.10	$\geqslant$2.48	$\geqslant$6.8	[18]
Ti^{3+}	$\geqslant$0.11	−3.5	8.20	0.040	−0.51	1.90	$\geqslant$3.9	[19]

[a] Oxidant in all cases was (ebbg)Ag^{III}; E° was taken as 0.32 V [14].
[b] Self-exchange rate for reductant.
[c] Log K_{12} for the cross reaction, evaluated as $(E^\circ_{ox} - E^\circ_{red})/0.059$.
[d] Sum of electrostatic work terms, evaluated from Eq. (7) in text.
[e] Second term in Eq. (6)/2.3.
[f] Values of k_{11} obtained by dividing $-d(Ag^{III})/dt$ by 2 (except for Ti(III) reaction) in consideration of stoichiometry.

with Eq. (6), lead to a calculated self-exchange rate of $10^{5.8\pm0.8}$ M^{-1} s^{-1} for (ebbg)Ag$^{III/II}$. Reflecting uncertainties in the rate of reduction by Cu^+ and in the formal potentials of Ti(III) species [19], experiments with these reductants yield only lower limits. Reduction by Cr(II) is not included in this treatment since rate constants for neither the Cr(II)–(ebbg)Ag^{III} reaction nor the $Cr^{2+/3+}$ self-exchange (only limits for each) are available. Because a major portion of the driving force for the reduction by $Fe(Me_2phen)_3^{2+}$ is presumably furnished by decomposition of the (ebbg)Ag^{II} intermediate, this reductant is likewise omitted.

Note that k_{11} for our Ag$^{III/II}$ couple is comparable to analogous values for a number of 4d and 5d systems (Table 5), but considerably greater than those pertaining to 3d-based couples, for which electron transfer tends to be associated with proportionately greater distortions of metal–ligand bonds as well as changes in coordination number and multiplicities. In addition, our value lies remarkably close to that reported for Ag$^{III/II}$ ($10^{5.6}$ M^{-1} s^{-1} [25] when these two states are stabilized via chelation by sulfonated tetraphenylporphyrin.

Our view that reductions of Ag(III) to Ag(I) in this ligand system take place most easily in successive 1e^- (rather than single 2e^-) exchanges appears to be in accord with earlier observations concerning this transformation. The oxidation of ascorbic acid (H_2A) to dehydroascorbic acid (A), Eq. (8), is a net-2e^-

$$H_2A + (ebbg)Ag^{III} \longrightarrow Ag^I + A + ebbgH^+ + H^+ \qquad (8)$$

transaction which proceeds rapidly [2d], but this reductant is known frequently to undergo oxidation in 1e^- steps [29]. Moreover, this conversion is further favored by the preliminary formation of an addition compound with the deprotonated form of the reductant, HA^-. The oxidation of hydrogen peroxide to O_2 (Eq.

Table 5
Electron self-exchange rates for transition metal complexes[a]

3d systems	Log k	4d systems	Log k	5d systems	Log k
$V(H_2O)_6^{3+/2+}$	−2.0	$Ru(NH_3)_6^{3+/2+}$	3.6	$IrCl_6^{2-/3-}$	5.3
$Cr(H_2O)_6^{3+/2+}$	−4.7	$Ru(bipy)_3^{3+/2+}$	8.6	$Os(phen)_3^{3+/2+}$	8.5
$Mn(H_2O)_6^{3+/2+}$	−3.5	$Mo(CN)_8^{3-/4-}$	4.5		
$Fe(H_2O)_6^{3+/2+}$	0.04	$Mo^{IV,III,III}/(Mo^{III})_3$	4.2[e]		
$Cu^{2+/+}$(aq.)	−5.0				
$Co(en)_3^{3+/2+}$	−4.7				
$Co(sep)^{3+/2+}$	0.7[b]				
$Cr^{IV/III}$	−0.5[c]				
$Cr^{V/IV}$	−6.1[c]				
$[VO(OH)]^{2+/+}$	−2[d]				

[a] Log k values pertain to 25 °C ($\mu = 1.0$ M) and are from Ref. [18] unless otherwise indicated.
[b] Sepulchrate complexes [26].
[c] Bis chelates of 2-ethyl-2-hydroxybutanoic acid [10].
[d] Ref. [27].
[e] Truncated cuboidal trinuclear molybdenum cations [28].

(9)) [2a] may likewise be taken to proceed through a pair of 1e^- acts in view of the known ability

$$H_2O_2 + (ebbg)Ag^{III} \longrightarrow Ag^{I} + O_2 + ebbgH^+ + H^+ \quad (9)$$

of H_2O_2 to partake in such steps [30][2].

Note that 2e^- transfers to (ebbg)Ag^{III} cannot be ruled out entirely. Neither formic acid nor ethanol is readily converted to a 1e^- oxidation product, and it has recently been shown [31] that both of these organics, as well as a number of additional alcohols, undergo oxidation by both $HCrO_4^-$ and by the more powerful acceptor [$Cr^{IV}O^{2+}$] (aq.) [32] by hydride transfer, an important mode for 2-unit oxidative changes involving C–H sites. It is reasonable to suppose that the oxidations, by Ag(III), of both formic acid [2b] and ethanol [2c] proceed by analogous paths, bypassing Ag(II) in these instances. However, these oxidations must surmount a substantial energy barrier, for they exhibit rates falling below that for the (ebbg)Ag^{III}–ascorbate reaction by 10^5–10^8 (under comparable conditions). A related 2e^- contribution may be envisaged for reduction by ascorbate but it would not compete detectably with the greatly favored two-step route.

Acknowledgements

Joint sponsorship of this work by the Donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the National Science Foundation (Grant 9314113) is gratefully acknowledged. We also thank Dr Edward Gelerinter for help in ESR measurements and Mrs Arla McPherson for technical assistance.

References

[1] (a) H.N. Po, *Coord. Chem. Rev., 20* (1976) 187; (b) W. Levason and M.D. Spicer, *Coord. Chem. Rev., 76* (1987) 95; (c) R.J. Lancashire, in G. Wilkinson (ed.), *Comprehensive Coordination Chemistry,* Vol. V, Pergamon, London, 1987, p. 849.

[2] (a) R. Banerjee, A. Das and S. Dasgupta, *J. Chem. Soc., Dalton Trans.,* (1989) 1645; (b) R. Banerjee, K. Das, A. Das and S. Dasgupta, *Inorg. Chem., 28* (1989) 585; (c) R. Banerjee, A. Das and S. Dasgupta, *J. Chem. Soc., Dalton Trans.,* (1990) 1207, 2271; (d) S. Dasgupta, E. Herlinger and W. Linert, *J. Chem. Soc., Dalton Trans.,* (1993) 567.

[3] (a) P. Ray and K. Chakravarty, *J. Indian Chem. Soc., 21* (1944) 47; (b) P. Ray, *Inorg. Synth., 6* (1960) 74.

[4] R.N. Bose and E.S. Gould, *Inorg. Chem., 24* (1985) 2832.

[5] E.R. Dockal and E.S. Gould, *J. Am. Chem. Soc., 94* (1969) 6673.

[6] (a) P.R. Guenther and R.G. Linck, *J. Am. Chem. Soc., 91* (1969) 3769; (b) R.G. Linck, *Inorg. Chem., 9* (1970) 2529.

[7] E.S. Gould and H. Taube, *J. Am. Chem. Soc., 86* (1964) 1318.

[8] (a) Y. Sasaki, R.S. Taylor and A.G. Sykes, *J. Chem. Soc., Dalton Trans.,* (1975) 396; (b) D.E. Linn, Jr., S.K. Ghosh and E.S. Gould, *Inorg. Chem., 28* (1989) 3225.

[9] A.H. Martin and E.S. Gould, *Inorg. Chem., 14* (1975) 873.

[10] M.C. Ghosh and E.S. Gould, *J. Am. Chem. Soc., 115* (1993) 3167.

[11] P.N. Dickson and D.W. Margerum, *Anal. Chem., 58* (1986) 3153.

[12] R.N. Banerjee and D. Banerjea, *Indian J. Chem., 17A* (1979) 246.

[13] G. Dulz and N. Sutin, *Inorg. Chem., 2* (1963) 917.

[14] (a) B. Chakravarty, *J. Inorg. Nucl. Chem., 41* (1979) 758; (b) K. Das, R. Banerjee, A. Das and S. Dasgupta, *Bull. Electrochem., 5* (1989) 477.

[15] (a) B.R. Baker, M. Orhanovic and N. Sutin, *J. Am. Chem. Soc., 89* (1967) 722; (b) J.C. Chen and E.S. Gould, *J. Am. Chem. Soc., 95* (1973) 5539.

[16] F.-R.F. Fan and E.S. Gould, *Inorg. Chem., 13* (1974) 2647.

[17] R.A. Marcus, *Discuss. Faraday Soc., 29* (1960) 21; *J. Phys. Chem., 67* (1963) 853.

[18] C. Creutz and N. Sutin, in J.J. Zuckerman (ed.), *Inorganic Reactions and Methods,* Vol. 15, VCH, Deerfield Beach, FL, 1986, pp. 13–51.

[19] B.S. Brunschwig and N. Sutin, *Inorg. Chem., 18* (1979) 1731.

[20] A.J. Bard, R. Parsons and J. Jordan (eds.), *Standard Potentials in Aqueous Solution,* Marcel Dekker, New York, 1985.

[21] W.H. Jolley, D.R. Stranks and T.W. Swaddle, *Inorg. Chem., 29* (1990) 1948.

[22] M. Chou, C. Creutz and N. Sutin, *J. Am. Chem. Soc., 99* (1977) 5615.

[23] G.M. Brown, H.J. Krentzein, M. Abe and H. Taube, *Inorg. Chem., 18* (1979) 3374.

[24] T.J. Meyer and H. Taube, *Inorg. Chem., 7* (1968) 2369.

[25] R. Langley, P. Hambright and R.F.X. Williams, *Inorg. Chim. Acta, 104* (1985) L25.

[26] I.I. Creaser, R.J. Geue, J. MacB. Harrowfield, A.J. Herlt, A.M. Sargeson, M.R. Snow and J. Springborg, *J. Am. Chem. Soc., 99* (1977) 3182.

[27] D.H. Macartney, *Inorg. Chem., 25* (1986) 2222.

[28] S.P. Ghosh and E.S. Gould, *Inorg. Chem., 32* (1993) 864.

[29] (a) E. Pelizzetti, E. Mentasti and E. Pramauro, *Inorg. Chem., 15* (1976) 2898; (b) A.M. Lannon, A.G. Lappin and M.G. Segal, *J. Chem. Soc., Dalton Trans.,* (1986) 619; (c) M.J. Akhtar and A. Haim, *Inorg. Chem., 27* (1988) 1608; (d) S.K. Ghosh and E.S. Gould, *Inorg. Chem., 28* (1989) 1538.

[30] J.K. Kochi, *Free Radicals,* Vol. 1, Wiley, New York, 1973, p. 627.

[31] S.L. Scott, A. Bakac and J.H. Espenson, *J. Am. Chem. Soc., 114* (1992) 4205.

[32] S.L. Scott, A. Bakac and J.H. Espenson, *J. Am. Chem. Soc., 113* (1991) 7787.

---

[2] Both this reaction and the related Ag^{III} oxidation of hydrazine to N_2 [2c] exhibit Ag^+-catalyzed paths. These are thought to involve intervention of Ag^0 and appear to be unrelated to the reactions at hand.