Kinetics of Oxidation of Ethanol, Isopropyl Alcohol, and Benzyl Alcohol by [Ethylenebis(biguanide)]silver(III) Cation in Aqueous Perchloric Acid Solutions

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In aqueous acid solutions, the complex $[Ag(H_2L)]^{3+}$ (H_2L = ethylenebis(biguanide)] quantitatively oxidises ethanol, isopropyl alcohol, and benzyl alcohol to the corresponding carbonyl products at moderate rate. The experimental rate law is $-d[\text{complex}]/dt = (k_1 + k_2/[H^+])[\text{alcohol}][\text{complex}]$. At 40 °C and $I = 1.0$ mol dm^{-3}, 10^5k_1 (dm^{-3} mol^{-1} s^{-1}) and 10^6k_2 (s^{-1}) values are: EtOH, 4.2 ± 0.3 and 2.8 ± 0.1; Pr^{i}OH, 7.5 ± 0.5 and 4.8 ± 0.2; PhCH$_2$OH, 95 ± 6 and 32.5 ± 2 respectively. The upper limit for the rate of reaction of $[Ag(H_2L)]^{3+}$ with methanol, t-butyl alcohol, ethylene glycol, and glycerol is the rate of autodecomposition of $[Ag(H_2L)]^{3+}$ and is less than 10% of the rate of oxidation of EtOH, Pr^{i}OH, or PhCH$_2$OH. Deprotonation of the alcohols assisted by axial co-ordination to $[Ag(H_2L)]^{3+}$ is suggested as a source of the inverse acid dependence. The whole reaction course is e.s.r. silent and a rate-determining C–H bond cleavage in the –CHOH group appears reasonable. Compared to other metal-ion oxidants, $[Ag(H_2L)]^{3+}$ appears to be the most selective reagent for PhCH$_2$OH.

The kinetics of oxidation of different alcohols by a large variety of reagents has been investigated[1–16] to elucidate structure–reactivity correlations, reaction mechanisms, and selectivity of the reagents. It has thus been observed that a thermodynamically stable metal complex is often a milder and more selective oxidant than the aquametal cations. Such complexes, however, have received only limited attention as oxidants for alcohols and the available kinetic data are scanty.

An interesting oxidant not previously reported for alcohols is the [ethylenebis(biguanide)]silver(III) cation (Figure), $[Ag(H_2L)]^{3+}$. This diamagnetic square-planar complex[17–19] cation is definitely known to contain low spin ($4d^8$) Ag^{3+} extensively stabilised (log $K \approx 52$)[20] by the acyclic ligand H_2L. The special stabilisation of d^8 ions (Ag^{3+}, Co^+) is common in square-planar complexes, although its extent seems fascinating with H_2L and $[Ag(H_2L)]^{3+}$ is a mild oxidant.

Reactions involving this complex are of interest in themselves because of the paucity of stable silver(III) species and also because true involvement of silver(III) in kinetics is rare. We report here the kinetics of oxidation of ethanol, isopropyl alcohol, and benzyl alcohol by $[Ag(H_2L)]^{3+}$ in acidic perchlorate media where the oxidant is reasonably stable against autodecomposition.[21] Under similar reaction conditions the upper limit for the rate of oxidation of methanol, t-butyl alcohol, ethylene glycol, and glycerol is the slow autodecomposition of $[Ag(H_2L)]^{3+}$. To our knowledge, there is no report on the kinetics of alcohol oxidation by any silver(III) species in acidic media, though kinetics of oxidation of some aliphatic alcohols by the anion $[Ag^{III}(H_2TeO_6)_2]^{5-}$ in strongly alkaline media have been investigated to a limited extent.[8]

Experimental

Materials.—Pure, diamagnetic crystals of [ethylenebis(biguanide)]silver(III) nitrate, $[Ag(H_2L)][NO_3]_3$, were prepared by a known method.[22,23] Methanol, ethanol, isopropyl alcohol, and benzyl alcohol were purified by refluxing with 2,4-dinitrophenylhydrazine (AnalaR) followed by distillation. The distillates were redistilled over freshly burnt lime. Ethylene glycol, glycerol, and t-butyl alcohol (all AnalaR) were used as received. All other materials were as used previously.[23,24]

Instrumentation.—Optical densities were measured on a Shimadzu Graphicord (UV-240) spectrophotometer. Magnetic susceptibility data and microanalytical data (C, H, and N) were obtained as described earlier.[23] E.s.r. spectra were run on reactant solutions containing up to 1.0 mmol dm^{-3} $[Ag(H_2L)]^{3+}$ and at varying stages in their decomposition under conditions where less than about 10^{-6} mol dm^{-3} $[Ag(bipy)_2]^{2+}$ (bipy = 2,2′-bipyridine) was detectable.

Product Analysis and Stoicheiometry.—The analyses were carried out under kinetic conditions when all $[Ag(H_2L)]^{3+}$ was consumed (optical density $\leqslant 0.01$ at 380 nm). Free ligand (H_2L) was isolated as sparingly soluble [ethylenebis(biguanide)]copper(II) sulphate which was quantitatively precipitated by the addition of ammoniacal copper(II) sulphate solution followed by a few drops of $[NH_4]_2SO_4$ solution.[25] The amount of Cu^{II} thus obtained was estimated iodometrically after the isolated copper(II) complex had decomposed. Silver(I) was precipitated as AgCl by the addition of dilute HCl and was estimated gravimetrically. The organic reaction products of EtOH, Pr^{i}OH, and PhCH$_2$OH were quantified as 2,4-dinitrophenylhydrazone derivatives.[26] For this purpose, Ag^+ was first quantitatively removed as AgCl, then a saturated solution of 2,4-dinitrophenylhydrazine in 2 mol dm^{-3} HCl was added and the mixture kept overnight at about 5 °C. After filtration, the precipitates were washed, dried, and weighed before and after recrystallisation from 80% methanol. The difference between the crude and the purified yield was 3—4% and the purified yield obtained in duplicate determinations were reproducible within 2—5%. The identities of the individual carbonyl products were ascertained by m.p. measurements of these derivatives.

Kinetic Measurements.—Using a sample quenching technique, the disappearance of $[Ag(H_2L)]^{3+}$ in reactions with alcohols was generally followed at 380 nm, the near-u.v. maximum (ε = 1 175 dm^{-3} mol^{-1} cm^{-1}) of the complex. Occasionally the reactions were followed also at 480 nm. At these wavelengths only the complex absorbs appreciably. The reaction temperature was controlled to within 0.1 °C using a closed type of thermostat inside which ambient light was almost absent. The

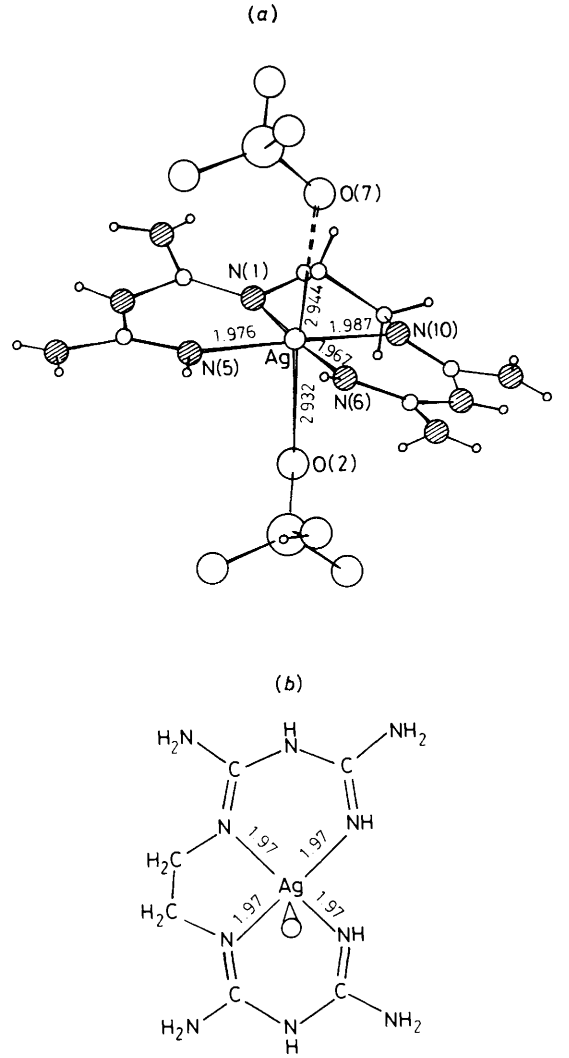

Figure. Structure of (*a*) $[Ag(H_2L)]SO_4[HSO_4]$[19] and (*b*) $[Ag(H_2L)][ClO_4]_3$.[18] Both have essentially the same square-planar structure with Ag–N bond lengths between 1.96 and 2.03 Å. Weak axial co-ordination by counter anion(s) are shown

ionic strength was maintained at $I = 1.0$ mol dm^{-3} by the addition of sodium perchlorate. A large excess ($\geqslant$ 100 fold) of the substrate alcohols and perchloric acid was used over the complex so that pseudo-first-order conditions were ensured. Pseudo-first-order rate constants k_0 were evaluated from the slopes of plots of $\log_{10} A$ *versus* time. A few experiments were run after the reaction media had been purged with purified N_2. Some were monitored in the presence of excess of ethylenebis(biguanide) (5 mmol dm^{-3}) and some in the presence of Ag^+ (up to 0.2 mol dm^{-3}). To assess any probable effect of ambient light on the reaction rate, the kinetics was also measured in reaction vessels exposed to ambient light. Initial complex concentrations were generally held at 0.2 mmol dm^{-3} except when the effect of complex concentration on rate was investigated.

All data except $\log_{10} A$ *versus* time plots were analysed by linear least-squares procedures where appropriate. Reported standard deviations in k_1, k_2, $\Delta H^\ddagger$, and $\Delta S^\ddagger$ values include propagated errors.

Results and Discussions

Stoicheiometry.—Recoveries of ethylenebis(biguanide) and Ag^+ were near quantitative: 95 ± 5 and 99 ± 2% respectively. The reactions were too slow to determine $|\Delta[\text{alcohol}]|/|\Delta[Ag^{III}]|$ using an excess of $[Ag(H_2L)]^{3+}$ over the concentrations of alcohols. However, $|\Delta[Ag^{III}]|/|\Delta[\text{carbonyl products}]|$ could be determined using a large excess of alcohol over the concentration of $[Ag(H_2L)]^{3+}$ in aqueous perchloric acid. The average of two independent measurements of this latter ratio were determined at 40 °C and [complex] = 5 mmol dm^{-3}, [alcohol] = 0.2—0.5 mol dm^{-3}, and $[H^+]$ = 0.1—0.2 mol dm^{-3}; ethanol, 1.09 ± 0.03; isopropyl alcohol, 1.02 ± 0.03; and benzyl alcohol, 1.06 ± 0.05. The blank reaction media (Ag^{III} absent) produced no oxidation of alcohols during the period allowed for the reaction. The consumption of $[Ag(H_2L)]^{3+}$ due to its autodecomposition[21] in acidified water did not exceed 10% of total decrease in $[Ag^{III}]$. While evaluating the stoicheiometry and also the percentage yield of H_2L, a small correction was applied to $[Ag^{III}]$ to allow for this. The recrystallized 2,4-dinitrophenylhydrazone derivatives melted within ±2 °C of their respective melting points reported in the literature.[27]

These results suggest that the main overall redox process is as in equation (1), with insignificant overoxidation or cleavage of

$$[Ag(H_2L)]^{3+} + R^1R^2CHOH \longrightarrow Ag^+ + H_2L + 2H^+ + R^1R^2CO \quad (1)$$

the alcohols to carboxylic acids. {At the experimental acidity, $[Ag^I(H_2L)]^+$ cannot exist and H_2L will be present in equilibrium with H_3L^+}. By comparison with the oxidation of simple alcohols by aqua-cations[4,12,13,28,29] and as benzaldehyde is the principal product of the oxidation of benzyl alcohol by permanganate ion,[30] a 1:1 stoicheiometry is expected in the present case. In general[4,31,32] oxidations of alcohols are faster than those of carbonyls. Moreover, use of much lower concentrations of the oxidant than of the alcohols minimizes,[33] at least kinetically, the possibility of further oxidation of carbonyl products. This was verified by deliberately doping the reaction media with 0.1—5 mmol dm^{-3} of carbonyl products (*i.e.* the maximum amount that may be formed in the reaction media). The values of k_0 in the presence and absence of added carbonyls were found to be practically identical.

Kinetics.—In the presence of a large excess of substrate alcohols (0.06—0.3 mol dm^{-3}), the disappearance of $[Ag(H_2L)]^{3+}$ obeyed first-order kinetics. Reactions were studied up to at least 70% (for slow reactions) and at most up to 90% completion (for faster reactions at higher temperature, higher [alcohol], and lower $[H^+]$). In all cases, plots of $\log_{10} A$ against time were very good straight lines. Replicate runs reproduced the individual pseudo-first-order rate constant k_0 within 2—7%. Under the experimental conditions, the autodecomposition[21] of the complex contributed less than 10% to the overall decay in concentration of Ag^{III}.

Dependence on complex concentration. The rate constant k_0 was found to be independent of the initial concentration of the complex. Thus, for alcohol concentration held constant at 0.1 mol dm^{-3} in 0.1 mol dm^{-3} $HClO_4$ but complex concentration varying in the range 0.1—0.8 mmol dm^{-3}, $10^6 k_0$ (s^{-1} values) at 40 °C, $I = 1.0$ mol dm^{-3} were: ethanol, 7.0 ± 0.3; isopropyl alcohol, 12.2 ± 0.6; and benzyl alcohol, 128 ± 6.

Dependence on $[H^+]$ *and* [alcohol]. At constant [alcohol] and $[ClO_4^-]$, plots of k_0 against $[H^+]^{-1}$ at every temperature were good straight lines [equation (2)] with regression coefficient

$$k_0 = C_1 + m_1/[H^+] \quad (2)$$

r better than 0.98. Again at fixed $[HClO_4]$ and $[ClO_4^-]$ in the temperature range 20—50 °C, k_0 shows a linear dependence ($r > 0.98$) on the alcohol concentration [equation (3)].

Table 1. First-order rate constants (k_0) under different experimental conditions. Ionic strength 1.0 mol dm^{-3} (NaClO$_4$)

Temperature/ °C	10^2[HClO$_4$]/ mol dm^{-3}	10^2[Alcohol]/ mol dm^{-3}	10^6k_0/s^{-1}	
			Exptl.	Calc.
		EtOH		
40	10	4	2.6	2.8
		8	6.0	5.6
		10	7.0^{a}	7.0
		12	9.2^{b}	8.4
		16	11.8	11.2
		20	15.2^{c}	14.0
		30	20.8^{d}	21.0
	4	30	33.3^{e}	33.6
	5		29.0	29.4
	6		26.3	26.6
	8		23.0	23.1
	15		18.0	18.2
	20		16.6	16.8
	10	4	5.5	5.6
		6	8.3	8.4
		8	11.2	11.2
		10	13.8	14.0
		14	19.5	19.4
		18	25.0	25.0
		20	28.0	27.8
45	4	30	67.2	67.4
	6		52.7	53.1
	8		45.8	46.0
	10		41.3	42.0
	15		35.0	36.0
	20		33.0	33.2
	25		31.0	31.6
50	10	4	11.3	12.7
		6	17.0	17.8
		8	22.7	24.0
		10	28.3^{e}	29.1
		14	39.7	40.0
		18	51.7	51.1
		20	55.3	57.0
	4	20	90.0	92.0
	8		61.2	62.7
	12		51.7	52.9
	16		46.7	47.0
	20		43.7	45.0
	30		39.8	41.0
		Pr^{i}OH		
40	10	4	4.8	5.0
		6	7.3	7.4
		8	9.8	9.8
	10	10	12.2^{a}	12.3
		12	14.7	15.0
		16	19.7	19.6
		20	24.5	25.1
	4	20	38.7	39.0
	6		30.8	31.0
	8		26.8	27.0
	12		22.8	23.0
	16		21.0	21.0
	20		19.7^{d}	19.8
45	10	2	4.3	4.5
		4	9.2	8.9
		6	13.7	13.3
		8	18.3	17.8
		12	27.7	26.6
		16	36.8	36.0
		20	44.3	44.4
	4	20	70.0	69.9
	6		55.8^{c}	55.7
	8		48.5	47.1
	12		41.5	41.5
	16		38.2	38.0
	20		36.0	35.8
50	10	2	7.8	8.0
		4	16.7	15.9
		8	31.7	31.8
		12	48.0	47.7
		20	80.0^{e}	79.5
		25	102.0	99.0
	4	20	125.0^{b}	123.0
	6		100.0	99.6
	8		87.5	89.1
	12		75.0	76.6
	16		68.8	68.3
	20		65.2	64.2
		PhCH$_2$OH		
20	10	10	16.8	16.1
		20	34.0	32.3
		30	47.8	48.4
		40	63.0	64.6
	2	30	107.0	108.5
	4		70.0	71.0
	6		57.0	58.5
	8		53.0	52.2
30	10	2	9.7	9.3
		4	19.2	18.7
		6	29.0	28.0
		8	38.2	39.4
	10	10	48.0	46.8
		15	70.2^{d}	70.2
		20	96.7	93.6
	2	15	152.0	150.0
	4		101.0	99.2
	8		75.3	75.3
	12		66.8	68.0
	16		62.7	62.6
	20		60.1	60.0
40	10	2	26.7	25.1
		4	51.7	50.3
		6	78.3	77.0
		8	103.0	100.0
		10	129.0^{a}	127.0
		15	197.0	191.0
	4	10	180.0	176.0
	5		153.0	160.0
	6		156.0	149.0
	8		139.0	136.0^{c}
	12		121.0	122.0
	20		111.0	111.0
45	10	2	45.0	42.3
		4	86.7	84.7
		6	124.0	127.0
		8	172.0^{b}	168.0
		10	210.0	212.0
	10	12	258.0^{e}	254.0
		15	327.0	318.0
	4	10	287.0	287.0
	5		262.0	262.0
	6		245.0	246.0
	8		225.0	225.0
	15		195.0	196.0
	20		187.0	188.0
50	10	2	70.0	70.0
		4	141.0	140.0
		5	178.0	175.0
		6	216.0	210.0
		8	283.0^{c}	280.0
		10	346.0	350.0
	4	10	470.0	467.0
	5		425.0	428.0
	6		408.0	402.0

Table 1 (*continued*)

Temperature/ °C	10^2[HClO$_4$]/ mol dm^{-3}	10^2[Alcohol]/ mol dm^{-3}	$10^6 k_0$/s^{-1}	
			Exptl.	Calc.
50	7	10	380.0	385.0
	8		370.0	369.0
	12		336.0	338.0
	20		312.0	312.0

Reaction conditions: unless otherwise stated, [complex] = 0.2 mmol dm^{-3}; wavelength of kinetic measurements, 380 nm, [a] [complex] varied from 0.1 to 0.8 mmol dm^{-3}. [b] These kinetics were repeated in the presence of (*i*) excess of ligand (5 mmol dm^{-3}), (*ii*) corresponding [carbonyl product] = 5 mmol dm^{-3}. [c] These kinetics were repeated in (*i*) the presence and in absence of ambient light, (*ii*) after purging with purified N_2. [d][AgClO$_4$] varied from 0.05 to 0.2 mol dm^{-3}. [e] These kinetics were repeated (*i*) in the presence of [Mn^{2+}] = 0.05 mol dm^{-3}, (*ii*) at 480 nm.

$$k_0 = m_2[\text{alcohol}] \qquad (3)$$

The reaction, therefore, appears to proceed through two concurrent paths both first order with respect to [complex] and [alcohol], but while one is independent of [H$^+$] the other exhibits an inverse acid dependence. The overall rate law is thus (4):

$$-\,\mathrm{d}[\mathrm{Ag(H_2L)^{3+}}]/\mathrm{d}t = k_0[\mathrm{Ag(H_2L)^{3+}}] = (k_1 + k_2/[\mathrm{H^+}])[\mathrm{Ag(H_2L)^{3+}}][\text{alcohol}] \qquad (4)$$

$$k_1 = C_1/[\text{alcohol}] \qquad (5)$$

$$k_2 = m_1/[\text{alcohol}] \qquad (6)$$

$$m_2 = (k_1 + k_2/[\mathrm{H^+}]) \qquad (7)$$

The k_1, k_2 values and the corresponding activation parameters are displayed in Table 2 and 3 respectively. In every case k_0 calculated [using equation (4)] from these k_1 and k_2 data agreed within 8% of the experimental k_0 value in Table 1.

Dependence on other factors. By working at constant [H$^+$] and [alcohol] the effects of added [Ag$^+$] (up to 0.20 mol dm^{-3}), [Mn^{2+}] (up to 0.05 mol dm^{-3}), ethylenebis(biguanide) (5.0 mmol dm^{-3}), and the organic product, *viz.*, carbonyl products (5 mmol dm^{-3}) were investigated at 40 °C. No effect was found. The value of k_0 remained practically unchanged also when the reactions were carried out under nitrogen or in the presence of ambient light (see Table 1).

E.S.R. Studies.—Under the experimental conditions where Ag$^{\text{II}}$ is detectable in concentrations less than about 10^{-6} mol dm^{-3},[34] the whole reaction course was e.s.r. silent.

Mechanism of Oxidation.—The complex ion is a weak acid[23] (pK_1 = 3.8 and pK_2 = 6.8 at 30 °C, I = 1.0 mol dm^{-3}) and in the experimental acidic solutions its undissociated form [Ag(H$_2$L)]$^{3+}$ predominates (>99.8%). Again, toward an extraneous reductant, the oxidative properties of metal-ion complexes in higher oxidation states decrease with decreased extent of protonation.[35] We, therefore, suggest the Scheme in which the observed inverse acidity dependence arises from the deprotonation of ROH assisted by its axial co-ordination to the complex.

$$[\mathrm{Ag(H_2L)}]^{3+} + \mathrm{R^1R^2CHOH} \overset{K_1}{\rightleftharpoons} \underset{(1)}{[\mathrm{Ag(H_2L)(R^1R^2CHOH)}]^{3+}} \qquad (8)$$

$$\underset{(1)}{[\mathrm{Ag(H_2L)(R^1R^2CHOH)}]} \overset{K_2}{\rightleftharpoons} \underset{(1)}{[\mathrm{Ag(H_2L)(R^1R^2CHO)}]^{2+}} + \mathrm{H^+} \qquad (9)$$

$$(1) \xrightarrow{k_1'} \mathrm{Ag^+} + \mathrm{H_2L} + \mathrm{R^1R^2CO} + 2\mathrm{H^+} \qquad (10)$$

$$(2) \xrightarrow{k_2'} \mathrm{Ag^+} + \mathrm{H_2L} + \mathrm{R^1R^2CO} + \mathrm{H^+} \qquad (11)$$

Scheme.

Small values[13] for the protonation constants K = [ROH$_2^+$]/[H$^+$][ROH] = 0.3—0.5 (depending on the alcohols) suggest that under the experimental acidity conditions [ROH$_2^+$] will be less than 7% of the total alcohol concentration. So unless ROH$_2^+$ is at least 5—10 times more active than ROH the former cannot have any appreciable effect on the overall reaction rate. It is assumed here that toward the cationic oxidant [Ag(H$_2$L)]$^{3+}$ the protonated alcohols ROH$_2^+$ are far less reactive than neutral ROH, as found in the oxidation of Pr^{i}OH by other cations.[4,12,13] Under the reasonable assumption (12), reactions (8)—(11) lead to the experimental rate law

$$(K_1[\mathrm{R^1R^2CHOH}] + K_1K_2[\mathrm{R^1R^2CHOH}]/[\mathrm{H^+}]) \ll 1 \qquad (12)$$

with k_1 and k_2 defined as in equations (13) and (14).

$$k_1 = K_1k_1' \qquad (13)$$

$$k_2 = K_1K_2k_2' \qquad (14)$$

Formation of inner-sphere adducts by alcohols, alkoxides, and mercapto compounds (RSH or RS$^-$) with metal complexes in acidic as well as in alkaline media is an established phenomenon.[9,10,36–40] Also, deprotonation occurs in alcohols co-ordinated to metal centres in higher oxidation states.[9,10] Moreover, *X*-ray structural studies[17,19] revealed axial coordination of SO$_4^{2-}$, NO$_3^-$, and even ClO$_4^-$ to [Ag(H$_2$L)]$^{3+}$. Hence, in aqueous alcoholic solutions, axial co-ordination by H$_2$O, its exchange with R^{1}R^{2}CHOH, and subsequent deprotonation of bound alcohol appear reasonable. Formation of such intimate complexes, however, does not prove (although it may suggest) that they react according to equations (10) and (11). The adducts (**1**) and (**2**) could be in equilibrium with the reactants and the products may form directly from reactants by an outer-sphere process. Anyway, we prefer an inner-sphere mechanism because of the moderately weak oxidising character of [Ag(H$_2$L)]$^{3+}$ as suggested by electrochemical studies.[41,42] Chakravarty[41] reports $E_{\frac{1}{2}}$ values for [Ag(H$_2$L)]$^{3+}$ to be 0.316 (Ag$^{\text{III}}$–Ag$^{\text{II}}$) and 0.156 V (Ag$^{\text{II}}$–Ag$^{\text{I}}$) respectively. Again, it has been proposed[43] that Cu$^{\text{III}}$ oxidises slowly, if at all, reductants which are not ligands in its inner sphere. Presuming similar mechanistic pathways for Cu$^{\text{III}}$ and (isoelectronic) Ag$^{\text{III}}$, reactions (10) and (11) are reasonable.

The e.s.r.-silent reaction course and the absence of any effect of Mn^{2+} or of dissolved O$_2$ indicates a non-radical process for the redox reactions (10) and (11). Photoelectron spectra established that little charge delocalisation takes place from the silver to the ligand in [Ag(H$_2$L)]$^{3+}$ and that this leaves the silver with a high positive charge[44] and electron affinity. A heterolytic fission of the C–H bond in the groups CHOH, therefore, seems probable in analogy with the favoured mechanisms for the oxidation of alcohols by lead tetra-acetate and chromic acid, in both of which the metal centre has a high electron affinity.

It is reasonable that the magnitudes of both K_1 and K_2 are much smaller than 1, so that $K_1K_2 \ll K_1$. Now, it is seen from Table 2 that k_1 is only about 15 times larger than k_2. So $k_2' \gg k_1'$ [see equations (13) and (14)]. This suggests that, toward cationic [Ag(H$_2$L)]$^{3+}$, alkoxide anions are more reactive than neutral alcohols.

Table 2. Rate constants for acid-independent (k_1) and -dependent (k_2) paths in the oxidation of alcohols by [ethylenebis(biguanide)]silver(III) ion

	$10^5\,k_1$/dm^{-3} mol^{-1} s^{-1}					$10^6\,k_2$/s^{-1}				
Alcohol	20	30	40	45	50 °C	20	30	40	45	50 °C
EtOH	—	—	4.2 ± 0.3	8.2 ± 0.5	16.7 ± 1	—	—	2.8 ± 0.1	5.7 ± 0.2	11.7 ± 0.4
$\mathrm{Pr^iOH}$	—	—	7.5 ± 0.5	13.7 ± 1	24.8 ± 2	—	—	4.8 ± 0.2	8.5 ± 0.3	15.0 ± 0.6
$\mathrm{PhCH_2OH}$	11.2 ± 0.5	33.3 ± 1.5	95 ± 6	162.5 ± 9	273 ± 6	5.0 ± 0.2	13.5 ± 0.6	32.5 ± 2	50 ± 2	77.7 ± 4

[complex] = 0.1—0.8 mmol dm^{-3}, [$\mathrm{HClO_4}$] = 0.04—0.3 mol dm^{-3}, [alcohol] = 0.02—0.3 mol dm^{-3}, I = 1.0 mol dm^{-3} ($\mathrm{NaClO_4}$).

Table 3. Activation parameters for k_1 and k_2 paths

	k_1 path		k_2 path	
Alcohols	$\Delta H^\ddagger$/ kJ mol^{-1}	$\Delta S^\ddagger$/ J K^{-1} mol^{-1}	$\Delta H^\ddagger$/ kJ mol^{-1}	$\Delta S^\ddagger$/ J K^{-1} mol^{-1}
EtOH	110 ± 22	18 ± 117	120 ± 8	26 ± 50
$\mathrm{Pr^iOH}$	99 ± 17	−12 ± 88	95 ± 11	−44 ± 59
$\mathrm{PhCH_2OH}$	82 ± 8	−39 ± 38	72 ± 12	−97 ± 34

Table 4. Relative rates of oxidation of EtOH, $\mathrm{Pr^iOH}$, and $\mathrm{PhCH_2OH}$ by metal-ion oxidants

	Relative rates			
Oxidant	EtOH	$\mathrm{Pr^iOH}$	$\mathrm{PhCH_2OH}$	Ref./Comments
$\mathrm{H_2CrO_4}$	1.0	0.9	2.1	32
$[\mathrm{Ag^{II}(2Me\text{-}py)}]^{2+}$ *	1.0	0.8	1.2	3
$[\mathrm{Cu^{III}(IO_6)_2}]^{7-}$	1.0	0.4	9.4	7
$[\mathrm{Ag^{III}(H_4TeO_6)_2(OH)_2}]^{3-}$	1.0	0.4	—	8
$[\mathrm{Ag^{III}(H_2L)}]^{3+}$	1.0	1.9	25	k_1 path } This
		1.7	12	k_2 path } work

* 2Me-py = 2-Methylpyridine.

It is noted that both k_1 and k_2 increase in the sequence EtOH < $\mathrm{Pr^iOH}$ ≪ $\mathrm{PhCH_2OH}$. The parameter k_1 ($= K_1k_1'$) and k_2 ($= K_1K_2k_2'$) are composite quantities and according to the proposed mechanism should be controlled by the ligating ability of the alcohols, acidity of the C–H bond in the CHOH group, and steric congestion in the ground and transition states. It is at best difficult to dissect these factors and to judge unambiguously their relative contributions in determining the observed sequence of k_1 and k_2.

One might find similar problems in interpreting the activation parameters (see Table 3). However, taken as a group, the activation enthalpies seem rather large and the entropies near zero (or at least not as negative as might be expected for associative substitution at other d^8 centres, say $\mathrm{Pt^{II}}$). These data might thus lend support to C–H bond breaking as the important process. Other arguments may also be advanced: a comparison[4,5] of activation entropies for the reagent-dependent associative substitution path involving similar gold(III) and platinum(II) systems shows that more positive $\Delta S^\ddagger$ is expected for metal centres bearing higher positive charge. In this context, near-zero activation entropies no longer appear unusual for an associative substitution process at the (d^8) silver(III) centre of a tripositive complex. It might be useful here to note that oxidation of $\mathrm{PhCH_2OH}$ and phenylethyl alcohol by $[\mathrm{Ni(bipy)_3}]^{3+}$ also involves rather high $\Delta H^\ddagger$ and near-zero $\Delta S^\ddagger$ values which Wells and Fox[6] interpret primarily to be an effect of the high charge borne by the complex cation. Perhaps comparison with redox or substitution reactions of other cationic silver(III) complexes would be helpful, but unfortunately there are no such data. Somewhat high $\Delta H^\ddagger$ values, as observed here, could also be a reflection of the weakly oxidising nature of the complex. Wells[5] observed that $\Delta H^\ddagger$ for a series of metal-ion oxidants may be roughly correlated with their thermodynamic oxidising strengths, $\Delta H^\ddagger$ increasing with decreasing reduction potential. Relative rates of oxidation of EtOH, $\mathrm{Pr^iOH}$, and $\mathrm{PhCH_2OH}$ by some metal-ion oxidants are collected in Table 4. Among these oxidants, $[\mathrm{Ag(H_2L)}]^{3+}$ oxidises $\mathrm{PhCH_2OH}$ most selectively.

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