Silver(III) Oxidation of the DL-Mandelate Ion

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The oxidation of DL-mandelate (MAN^-) by $[Ag(OH)_4]^-$ in strongly alkaline media has been investigated by stopped-flow spectrophotometry. Product analysis shows that benzaldehyde is the sole organic product when MAN^- is in excess. The rate law is $k_{obs} = (a + b[OH^-])[MAN^-]$, where $a = (6.2 \pm 0.2)$ dm^3 mol^{-1} s^{-1} and $b = (7.0 \pm 0.3)$ dm^6 mol^{-2} s^{-1} at 25 °C and $I = 1.3$ mol dm^{-3}. Oxidation of benzaldehyde (to benzoic acid) by Ag^{III} is more than an order of magnitude slower than the mandelate reaction. Activation parameters for both hydroxide-dependent and -independent paths are $\Delta H_a^\ddagger = (59.3 \pm 2.1)$ kJ mol^{-1}, $\Delta S_a^\ddagger = (-32.0 \pm 0.5)$ J mol^{-1} K^{-1} and $\Delta H_b^\ddagger = (48.0 \pm 2.3)$ kJ mol^{-1}, $\Delta S_b^\ddagger = (-68.5 \pm 0.6)$ J mol^{-1} K^{-1}, respectively. Two different mechanistic pathways are discussed. A base-catalysed process, followed by C–C cleavage, seems to be the most probable mode of decarboxylation. The comparative non-reactivity of phenylglyoximate and α-methoxyphenylacetate ions underlines the importance of the α-OH group in the mandelate oxidation.

The reactions of α-hydroxy carboxylic acids and their salts with metal-ion complexes have been extensively studied in the past decade.[1–12] Because of their importance in biological systems,[5] the understanding of the complexation and degradation (oxidation) patterns of these hydroxylated acids can open new routes to homogeneous catalysis, biochemical synthesis and biotechnology.[5]

Vanadium(V) complexes of glycolic, L-lactic, L-mandelic, DL-glyceric, DL-chlorolactic, L-phenyllactic and L-malic acids have recently been studied by NMR spectroscopy.[1] All except L-phenyllactic acid form two major complexes at pH values between 2.5 and 7. In the case of L-phenyllactic acid, only one complex was reported. The study also showed that all the acids act as bidentate ligands. On the other hand, Fan and Gould[6] have successfully prepared monodentate Co^{III} complexes of mandelic and lactic acids in perchlorate media.

Numerous studies in the oxidation of α-hydroxycarboxylic acids and their complexes are reported in the literature.[4,7–12] For instance, the RuO_4^{2-}-catalysed oxidation of malate and mandelate ions by hexacyanoferrate(III) in aqueous alkaline media is first order in RuO_4^{2-} and zero order in oxidant, and proceeds *via* formation of a complex between substrates and ruthenate ion.[4] Redox reactions of Co^{III}-bound complexes of α-hydroxyacids ($[(NH_3)_5Co–L]^{2+}$, L = mandelic or lactic acid) have also been studied.[9,10] Kalidoss and Srinivasan[11] reported that the addition of oxalic acid enhances the rate of Cr^{VI} oxidation of $[(NH_3)_5Co–L]^{2+}$ complexes of mandelic and lactic acids. Product analysis shows that the reaction proceeds *via* (*i*) a ternary cyclic intermediate to give benzaldehyde and acetaldehyde, respectively, and (*ii*) an acyclic transient route leading to the formation of α-keto compounds.

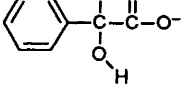
Although Walling and Amarnath[12] found only benzaldehyde in the reaction of Fenton's reagent (Fe^{2+}, H_2O_2) with mandelic acid, Mahapatro *et al.*[13] showed that phenylglyoxylic acid is also formed.

The tetrahydroxoargentate(III) ion is a d^8, diamagnetic, square-planar complex which can undergo both substitution and redox reactions.[14,15] It is prepared electrolytically at a silver anode in 1.2 mol dm^{-3} NaOH and has a half-life of *ca.* 90 min at room temperature and a UV absorption maximum at 267 nm (ε = 1.17 × 10^4 dm^3 mol^{-1} cm^{-1}).[16] It rapidly decomposes in acidic media *via* the aquated species $Ag(OH)_3H_2O$ with a rate constant of 140 s^{-1}.[17]

Substitution reactions of $[Ag(OH)_4]^-$ with various inorganic and organic ligands, including *vic*-dioximate ligands [dimethylglyoximate (dmg), diphenylglyoximate (dpg), cyclohexane-1,2-dione dioximate (chdd)],[18] nicotinamide,[19] periodate,[14] tellurate,[14] triglycine[20] and tetraglycine,[20] have been studied in the present authors' laboratory. In the case of periodate and tellurate, the kinetically stable complexes $[Ag(H_2IO_6)_2]^{3-}$ and $[Ag(H_4TeO_6)_2]^-$ were obtained. Coloured bis-chelate complexes of Ag^{III} with dmg, dpg and chdd were successfully prepared by direct mixing of $[Ag(OH)_4]^-$ and the ligands in alkaline solution.[18] These complexes are stable for several minutes before undergoing internal redox. The decreasing order of stability is from chdd to dpg. In general, $[Ag(OH)_4]^-$ substitution reactions are inferred to proceed *via* an associative mechanism.

Redox reactions of $[Ag(OH)_4]^-$ with potentially complexing substrates such as ethylenediamine (en),[21] HO_2^-,[22] $S_2O_3^{2-}$,[23] 4-t-butylphenolate,[24] hypophosphite,[25] biuret,[19] thiourea,[26] iodide,[27] azide[28] and thiocyanate[29] ions have also been studied. In the particular case of 4-t-butylphenolate, the reaction follows a biphasic pattern, corresponding to two sequential one-electron reductions of the metal.[24] Intermediate inner-sphere complexes were detected in the reduction of thiosulphate and azide by $[Ag(OH)_4]^-$.[22,23]

In this paper, we report the results of a study of the reduction of Ag^{III} by mandelate (MAN^-, **1**) ion in alkaline media. In order to justify the conclusions, we have also investigated the reactions of Ag^{III} with benzaldehyde, α-methoxyphenylacetate (MPA^-, **2**) and phenylglyoxylate (PG^-, **3**) ions.



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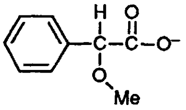

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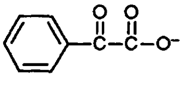

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Experimental

Reaction Solutions.—The tetrahydroxoargentate(III) complex ion was prepared as previously described.[15,24,27] $[Ag(OH)_4]^-$ solutions were prepared at high current density by electrolysis at a silver foil anode of 1.2 mol dm^{-3} NaOH (*ca.* 200 cm^3) in a 250 cm^3 polyethylene beaker. Argon gas was bubbled through the solution to exclude oxygen and carbon dioxide and to provide

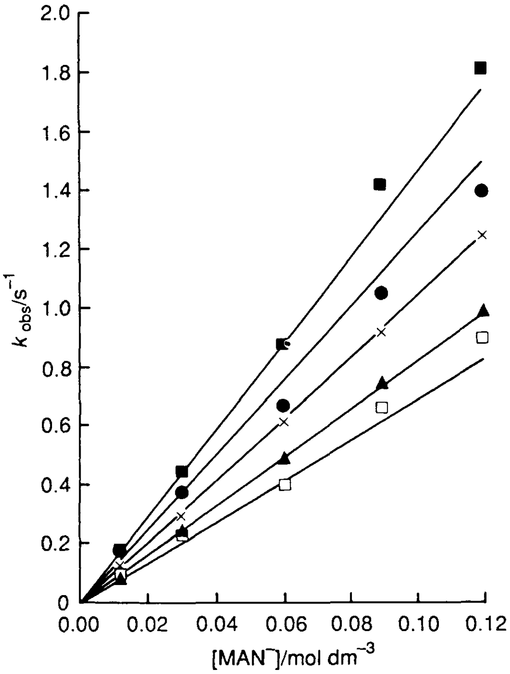


Figure 1. Plots of observed pseudo-first-order rate constants *versus* [MAN$^-$] at different [OH$^-$]. □, 0.12 mol dm^{-3}; ▲, 0.3 mol dm^{-3}; **X**, 0.6 mol dm^{-3}; ●, 0.9 mol dm^{-3}; ■, 1.2 mol dm^{-3}. I = 1.3 mol dm^{-3}; T = 25 °C. Solid lines are calculated from least-squares fit of all data [eqn. (2)].

constant stirring of the solution. After electrolysis, solutions were filtered with an all-glass filtration apparatus[30] to remove solid silver oxides.

All mandelate reaction solutions were freshly made in doubly distilled water or in 1.2 mol dm^{-3} sodium perchlorate from a 0.6 mol dm^{-3} stock solution prepared as follows: a solution of NaOH, standardized with reagent grade oxalic acid (Matheson Coleman & Bell), was used to titrate a known amount of recrystallized[31] mandelic acid (Matheson Coleman & Bell). The amount of mandelic acid needed was then calculated, exactly weighed, dissolved in an equivalent amount of standardized NaOH and brought to the appropriate volume with water. Benzaldehyde (Fisher), sodium α-methoxyphenylacetate (Aldrich) and sodium phenylglyoxylate (Aldrich) were used as received without any further purification. Solutions of benzaldehyde were made in doubly distilled water by measuring out the required volume of the reagent. NaPG and NaMPA solutions were prepared by weight. Sodium hydroxide solutions (1.2 mol dm^{-3}) were prepared from 50% low-carbonate NaOH (Fisher). A 1.2 mol dm^{-3} (or 6 mol dm^{-3}) $NaClO_4$ solution was used for ionic strength adjustment when appropriate. $NaClO_4$ was prepared from 50% NaOH and $HClO_4$ (Fisher) adjusted to pH 7, followed by filtration.[27]

An Aminco–Morrow stopped-flow apparatus was used in the kinetic runs. Large excesses of reductant were used for all experiments. Because of the high absorbance of mandelate in the vicinity of the $[Ag(OH)_4]^-$ maximum absorbance peak (267 nm), kinetics were generally monitored at 300 nm as $[Ag(OH)_4]^-$ disappearance. At this wavelength, the reductant did not show any significant absorbance. The reaction was followed on a Tektronix 564B storage oscilloscope coupled to a Tandy TRS-80 microcomputer.[26] Kinetic data were processed on a PC computer using the OLIS kinetic fitting (Kinfit) program.[32] All reaction traces gave excellent first-order fit and replicate runs were reproducible to within 5%. Total ionic strength was maintained at 1.3 mol dm^{-3} for all experiments. Temperature control was to within ±0.1 °C at 25 °C and ±0.2 °C for other temperatures. Spectral analyses were performed on an HP 8451 diode array spectrophotometer.

Results

Product Analysis.—Known concentrations of $[Ag(OH)_4]^-$ and mandelate (in excess) were allowed to react to completion (discharge of colour). Immediately after the discharge, a strongly acidic (HCl, Ashland) solution of 2,4-dinitrophenylhydrazine (J. T. Baker) was added to the reaction mixture.[33] Precipitation of an orange 2,4-dinitrophenylhydrazone (2,4-DNP) was observed. The precipitate was left overnight, then filtered and dried. The melting point confirmed the 2,4-DNP of benzaldehyde (m.p. 236.5–237.0 °C), indicating that benzaldehyde is a product of the reaction. When blank solutions of mandelate were treated with 2,4-dinitrophenylhydrazine, no precipitate was observed.

In some systems, there is evidence of formation of phenylglyoxylic acid or PG$^-$ in addition to benzaldehyde in the oxidation of mandelic acid.[11,13,34] However, in the present study, attempts to identify PG$^-$ as a product following the method of Mahapatro *et al.*[13] gave negative results. In addition, if PG$^-$, which is stable in base and absorbs strongly at λ = 300 nm, were forming, kinetic observations of the reaction of mandelate and Ag^{III} would have been affected as the concentration of PG$^-$ was building up. This was not the case. Also, if PG$^-$ were a product, its 2,4-DNP melting point (195 °C)[13] would have interfered with the melting point reported above.

In the light of all the above evidence, it is concluded that the sole product of the reaction is benzaldehyde.

Stoichiometry of the Reaction.—The reaction stoichiometry was determined at excess Ag^{III} by measuring the difference between initial and final absorbances in the stopped-flow apparatus. The values for Δ[Ag^{III}] thus obtained, when compared with the amount of mandelate present, indicated a stoichiometry of 1:1 (Table 1). Under these conditions of excess Ag^{III}, a slower, second reaction is observed which can be attributed to the oxidation of benzaldehyde to benzoate ion. In separate experiments, benzaldehyde was reacted with Ag^{III}. The specific rate is about fifteen times slower than that of the Ag^{III}–mandelate system. This is an indication that there is no interference from the benzaldehyde reaction under the conditions of the kinetic experiments. After acidification, the product spectrum was identical with that of a solution made from solid benzoic acid.

According to the stoichiometry obtained at excess oxidant and the product analysis, the overall reaction is that shown in eqn. (1). When excesses of mandelate are added to $[Ag(OH)_4]^-$,

$$PhCH(OH)CO_2^- + [Ag(OH)_4]^- + OH^- \longrightarrow PhCHO + [Ag(OH)_2]^- + CO_3^{2-} + 2H_2O \quad (1)$$

its yellow colour is immediately discharged accompanied by the characteristic odour of benzaldehyde, consistent with eqn. (1). The mixture then turns black within 3 to 5 s as solid silver oxide precipitates.

Kinetics.—The dependence of the reaction rate on mandelate ion concentration (0.012 mol dm^{-3} $\leqslant$ [MAN$^-$] $\leqslant$ 0.12 mol dm^{-3}) was studied at 25 °C, I = 1.3 mol dm^{-3}, 0.12 mol dm^{-3} $\leqslant$ [OH$^-$] $\leqslant$ 1.2 mol dm^{-3}, with initial silver concentrations ranging from 5×10^{-4} to 1×10^{-3} mol dm^{-3}. The kinetics exhibit a first-order behaviour in $[Ag(OH)_4{}^-]$ and are dependent on hydroxide concentrations. No change in rate constants was observed when the reaction was studied at wavelengths varying from 280 to 450 nm. Plots of the observed

Table 1. Stoichiometry of the reaction of DL-mandelate with Ag^{III}.

$[Ag^{III}]_0 \times 10^4$/mol dm^{-3}	$[MAN^-]_0 \times 10^4$/mol dm^{-3}	$\Delta[Ag^{III}] \times 10^4$/mol dm^{-3}	$\Delta[Ag^{III}]/\Delta[MAN^-]$
8.2	7.2	6.9	0.96
7.6	5.2	6.61	1.2
9.76	6.0	6.62	1.1
10.2	8.4	8.1	0.96
			Average 1.05 ± 0.10

Table 2. Variation of rate parameters[a] with temperature at different $[OH^-]$; $[MAN^-] = 0.06$ mol dm^{-3}, $I = 1.3$ mol dm^{-3}.

T/°C	a/dm^3 mol^{-1} s^{-1}	b/dm^6 mol^{-2} s^{-1}
15	2.21 ± 0.01	3.28 ± 0.01
25	5.82 ± 0.60	6.94 ± 0.70
31	9.08 ± 0.40	8.95 ± 0.50
40	16.7 ± 0.40	18.5 ± 0.4
45	27.4 ± 1.3	23.4 ± 1.5

$\Delta H_a^\ddagger = (59.3 \pm 2.1)$ kJ mol^{-1} $\Delta H_b^\ddagger = (48.0 \pm 2.3)$ kJ mol^{-1}
$\Delta S_a^\ddagger = (-32.0 \pm 0.5)$ J mol^{-1} K^{-1} $\Delta S_b^\ddagger = (-68.5 \pm 0.6)$ J mol^{-1} K^{-1}

[a] Eqn. (2).

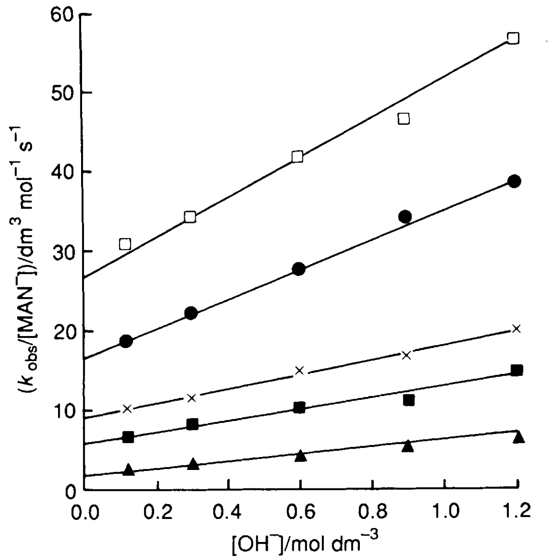


Figure 2. Hydroxide dependence at different temperatures for the Ag^{III}–mandelate reaction. ▲, $T = 15$ °C; ■, $T = 25$ °C; X, $T = 31$ °C; ●, $T = 40$ °C; □, $T = 45$ °C; $[MAN^-] = 0.06$ mol dm^{-3}; $I = 1.3$ mol dm^{-3}. The solid lines are calculated using the activation parameters from the least-squares fit of the data at all temperatures [eqn. (3), Table 2].

pseudo-first-order rate constants *versus* $[MAN^-]$ give a family of straight lines which pass through the origin (Fig. 1). When the slopes of these lines are plotted against hydroxide concentrations, a straight line with a significant intercept is obtained. Hence, the empirical rate law can be written as eqn. (2). A linear

$$-\frac{d[Ag(OH)_4{}^-]}{dt} = k_{obs}[Ag(OH)_4{}^-] \qquad (2)$$

$$= (a + b[OH^-])[MAN^-][Ag(OH)_4{}^-]$$

least-squares treatment of all the data gives $a = (6.2 \pm 0.2)$ dm^3 mol^{-1} s^{-1} and $b = (7.0 \pm 0.3)$ dm^6 mol^{-2} s^{-1}.

Activation Parameters.—In order to determine activation parameters, the reaction was carried out at different temperatures in the range 15–45 °C, at $[MAN^-] = 0.06$ mol dm^{-3}, $I = 1.3$ mol dm^{-3}, and at all hydroxide concentrations. Plots of $k_{obs}/[MAN^-]$ *versus* hydroxide concentration are linear with non-zero intercepts (Fig. 2). $\ln(aNh/RT)$ and $\ln(bNh/RT)$ are both linear functions of $1/T$ in accordance with eqn. (3).[35] Least-

$$k = \left(\frac{RT}{Nh}\right)\exp\left(\frac{-\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R}\right) \qquad (3)$$

$$(k = a \text{ or } b)$$

squares values of the enthalpy and entropy of activation for the two paths are included in Table 2.

Discussion

Mandelic acid and its salts have been reported to form both mono- and bi-dentate complexes with transition metal ions.[10,12] In this study there is no spectral or kinetic evidence of an inner-sphere complex formation between $[Ag(OH)_4]^-$ and mandelate. However, rapid formation of monodentate or/and bidentate metal–mandelate intermediates have been observed in other systems. For instance, McAuley and Brubaker reported that the oxidation of mandelic acid by Ce^{IV} in aqueous sulphuric acid involves the intermediate formation of a complex adduct between the metal and the α-hydroxy acid.[36] The involvement of five-co-ordinate Ag^{III} intermediate adducts in $[Ag(OH)_4]^-$ redox and complexation reactions is well established.[23,25,27] Spectral evidence for four-co-ordinate complex intermediates in Ag^{III} redox reactions can be found in its reduction by thiosulphate[23] and azide.[28]

The empirical rate law obtained in eqn. (2) can result from two distinctive mechanisms, depending on whether interaction with OH^- occurs before or after interaction between oxidant and reductant.[37,38] The first mechanism [eqns. (4)–(6)] involves a rapid equilibrium association between Ag^{III} and MAN^- [eqn. (4)]. The resulting intermediate decomposes in two rate-determining steps either by undergoing internal redox [eqn. (5)] or by a base-catalysed process [eqn. (6)] to give the products shown in eqn. (1).

Mechanism 1

$$[Ag(OH)_4]^- + PhCH(OH)CO_2{}^- \underset{\text{fast}}{\overset{K_e}{\rightleftharpoons}} \text{intermediate} \qquad (4)$$

$$\text{intermediate} \xrightarrow[\text{slow}]{k_1} \text{products} \qquad (5)$$

$$\text{intermediate} + OH^- \xrightarrow[\text{slow}]{k_2} \text{products} \qquad (6)$$

The pseudo-first-order rate constant for this system of parallel reactions is

$$k_{obs} = \frac{(k_1K_e + k_2K_e[OH^-])[MAN^-]}{1 + K_e[MAN^-]} \qquad (7)$$

Assuming that $K_e[\mathrm{MAN}^-] << 1$, eqn. (7) reduces to

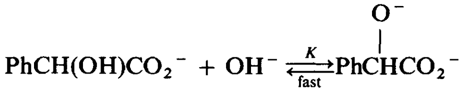
$$k_{obs} = (k_1K_e + k_2K_e[\mathrm{OH}^-])[\mathrm{MAN}^-]$$

which has the same form as the empirical rate law in eqn. (2) [$a = k_1K_e = (6.2 \pm 0.2)\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$; $b = k_2K_e = (7.0 \pm 0.3)\ \mathrm{dm^6\ mol^{-2}\ s^{-1}}$].

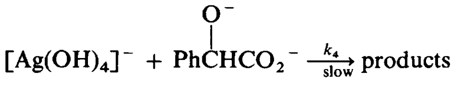
In the second possible mechanism [eqns. (8)–(10)], $[\mathrm{Ag(OH)_4}]^-$ reacts in parallel paths with singly and doubly deprotonated ions.

Mechanism 2

$$[\mathrm{Ag(OH)_4}]^- + \mathrm{PhCH(OH)CO_2}^- \xrightarrow[\text{slow}]{k_3} \text{products} \qquad (8)$$



$$\mathrm{PhCH(OH)CO_2}^- + \mathrm{OH}^- \underset{\text{fast}}{\overset{K}{\rightleftharpoons}} \mathrm{Ph}\overset{\mathrm{O^-}}{\overset{|}{\mathrm{C}}}\mathrm{HCO_2}^- \qquad (9)$$



$$[\mathrm{Ag(OH)_4}]^- + \mathrm{Ph}\overset{\mathrm{O^-}}{\overset{|}{\mathrm{C}}}\mathrm{HCO_2}^- \xrightarrow[\text{slow}]{k_4} \text{products} \qquad (10)$$

The rate constant obtained from this mechanism is

$$k_{obs} = \frac{(k_3 + k_4K[\mathrm{OH}^-])[\mathrm{MAN}^-]_T}{1 + K[\mathrm{OH}^-]} \qquad (11)$$

where $[\mathrm{MAN}^-]_T$ is the total concentration of mandelate.

The experimental value of $\mathrm{p}K_{a2}$ for mandelic acid is *ca.* 16.[39] The equilibrium constant (K) of reaction (9) is thus estimated to be $\approx 10^{-2}$. Using the highest hydroxide concentration in this study (1.2 mol dm^{-3}), the maximum value of $K[\mathrm{OH}^-]$ is 0.012, which is much smaller than unity. Hence, eqn. (11) reduces to eqn. (12), which is in accord with the experimental rate law [a =

$$k_{obs} = (k_3 + k_4K[\mathrm{OH}^-])[\mathrm{MAN}^-]_T \qquad (12)$$

$k_3 = (6.2 \pm 0.2)\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$; $b = k_4K = (7.0 \pm 0.3)\ \mathrm{dm^6\ mol^{-2}\ s^{-1}}$, $k_4 \approx 7.0 \times 10^2\ \mathrm{dm^6\ mol^{-2}\ s^{-1}}$].

The absence of kinetic terms containing a $1/[\mathrm{OH}^-]$ dependence is an indication that there is no equilibrium replacement of a silver(III) hydroxyl by the reductant. Thus, even though an expansion of the metal co-ordination sphere is likely in both mechanisms, ligand exchange is not kinetically significant prior to the redox step. Terms linearly dependent on $[\mathrm{OH}^-]$ have been observed in other systems, including the reactions of $[\mathrm{Ag(OH)_4}]^-$ with ethylenediamine,[21] $\mathrm{HO_2}^-$,[22] thiourea[26] and hypophosphite ion.[25] In all four of these reactions, however, substrate deprotonation, as in mechanism 2, could be ruled out. For the first three cases, calculated bimolecular rate constants (analogous to k_4) would exceed the diffusion-controlled limit, while in the case of hypophosphite,[25] the measured activation parameters for silver(III) reaction were lower than for ligand deprotonation itself. For the mandelate system, however, the calculated value of k_4, while two orders of magnitude larger than k_3, is not unreasonable. Hence, in the present case, we are unable to choose between the two alternative mechanisms.

Reduction of $\mathrm{Ag^{III}}$ can involve either a two-electron change or sequential one-electron processes. Radical involvement has been reported[40] in the reactions of α-hydroxy carboxylic acids with various metal ions *via* eqns. (13)–(15). However, if long-lived radical intermediates were forming during the course of the $\mathrm{Ag^{III}}$–MAN^- reaction, a deviation from 1:1 stoichiometry and/or a biphasic reaction would be expected.[24] This mechanism does not add any insight into the presence of a hydroxide path in the rate law proposed here. Therefore, the authors do not believe that reactions (13)–(15) are important when $\mathrm{Ag^{III}}$ is the oxidant. This is consistent with most other $[\mathrm{Ag(OH)_4}]^-$ reactions for which a simultaneous two-electron reduction to $\mathrm{Ag^I}$ seems to be preferred.

$$\mathrm{RCH(OH)CO_2}^- + \mathrm{ox} \longrightarrow \mathrm{ox}^{\bullet} + \mathrm{RCH(OH)CO_2}^{\bullet} \qquad (13)$$

$$\mathrm{RCH(OH)CO_2}^{\bullet} \longrightarrow \mathrm{R\dot{C}HOH} + \mathrm{H}^+ + \mathrm{CO_2} \qquad (14)$$

$$\mathrm{R\dot{C}HOH} \longrightarrow \mathrm{RCHO} + \mathrm{H}^+ + \mathrm{e}^- \qquad (15)$$

In order to justify the proposed mechanisms, additional experiments were conducted with sodium α-methoxyphenylacetate (NaMPa) and sodium phenylglyoxylate (NaPG). In the case of NaMPA, there was no acceleration of the rate of $[\mathrm{Ag(OH)_4}]^-$ decomposition over that in the absence of substrate, even at the highest substrate concentration (0.12 mol dm^{-3}). Hence, the rate of this reaction is estimated to be at least two orders of magnitude smaller than the rate for both hydroxide-dependent and -independent paths in the mandelate reaction. This is in agreement with both mechanisms 1 and 2, in which deprotonation of the α-hydroxy group is important.

Similarly, the observed constants for the reaction of $[\mathrm{Ag(OH)_4}]^-$ with NaPG are within experimental error of those of blank solutions, thus stressing the involvement of the hydroxide group and arguing against PG^- as an intermediate in the mandelate reaction. The non-reactivity of MPA^- and PG^- provides further support for the absence of a free radical mechanism [eqns. (13)–(15)] in which the carboxylate group provides the first electron.

In the light of all the above, intimate mechanistic schemes can be considered. While the mechanism given in eqns. (4)–(6) requires intimate contact between oxidant and reductant, it seems likely that eqns. (8) and (10) also involve intermediates containing five-co-ordinate $\mathrm{Ag^{III}}$. Scheme 1 depicts the likely reaction sequence for the path corresponding to eqn. (6). While deprotonation of the α-OH seems also to be important in the hydroxide-independent path [eqns. (4) and (5), which are equivalent to eqn. (8)], the proton can be transferred either to the solvent or, as shown in Scheme 2, to a bound OH^-.[25]

The activation parameters observed here are similar to those reported for other α-hydroxycarboxylic acid reactions with metal ions which also go by complexation mechanisms.[3,8] For a C–C fission, as is the case in this study, higher enthalpy values might be expected. The more favourable activation parameters obtained are indicative of formation of an intermediate in the intimate step of the reduction process. This is in accord with the lack of reactivity of the mandelate analogues NaMPa and NaPG, where the hydroxide sites are blocked by methyl and keto groups, respectively.

Electron movement in schemes similar to Schemes 1 and 2 have been reported in several α-hydroxy acid decarboxylations.[9,36] In α-hydroxy carboxylic acid reactions leading to the formation of keto products, a C–H fission in the transition state complex is inferred.[13] On the other hand, systems that generate aldehydes proceed *via* a C–C cleavage.[2,10,41] Reactions that yield both aldehydes and keto products are thought to go *via* both modes of oxidation.[9,11] The lack of evidence of any keto product formation in the present reaction leads us to conclude that a C–C bond fission is the most probable mode for decarboxylation of DL-mandelate by $\mathrm{Ag^{III}}$.

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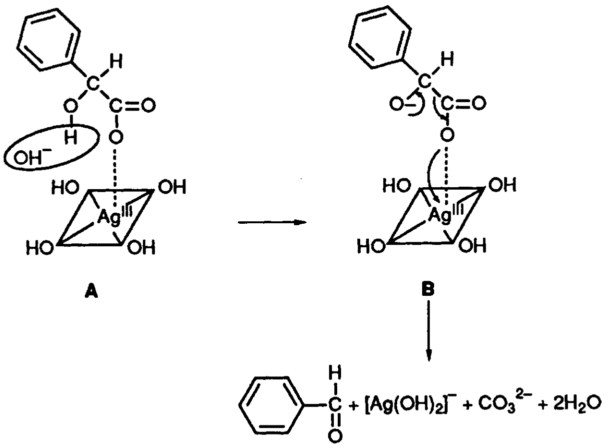
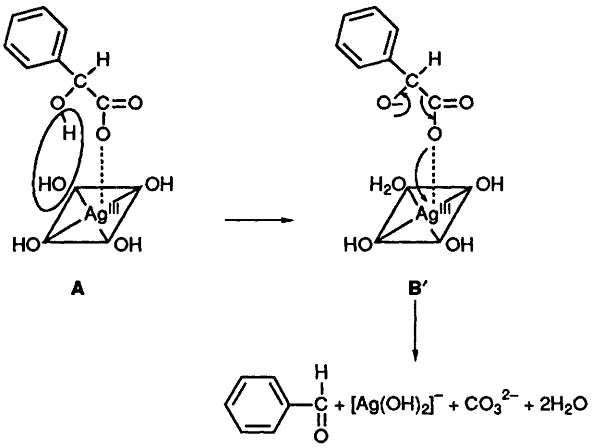


Scheme 1.



Scheme 2.

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