Kinetics and Mechanism of the Reaction between 4-t-Butylphenolate Anion and Tetrahydroxoargentate(III) in Aqueous Alkaline Media

Rama K. Panda and Louis J. Kirschenbaum *
Department of Chemistry, University of Rhode Island, Kingston, R.I. 02881, U.S.A.

The reaction of $[Ag(OH)_4]^-$ with 4-t-butylphenolate (L^-) follows a biphasic absorbance change, each phase exhibiting pseudo-first-order kinetics under limiting conditions of the silver(III). A subsequent, slow, and very small absorbance increase ($t_{0.5} > 1$ h) is accompanied by the precipitation of metallic silver. In the $[L^-]$ range $0.5 \times 10^{-3} - 10 \times 10^{-3}$ and $[OH^-]$ range 0.12—1.2 mol dm^{-3} at 25 °C and in aqueous medium, the pseudo-first-order rate constant for the initial, faster phase, k_f (in s^{-1}), corresponds to the first one-electron transfer from L^- to the initial silver(III) species and obeys the relation (i). The pseudo-first-order rate constant for the second,

$$k_f = (0.330 \pm 0.09) + (1.26 \pm 0.09) \times 10^3[L^-] + (2.64 \pm 0.28) \times 10^2[L^-]/[OH^-] \qquad \text{(i)}$$

slower phase, k_s (in s^{-1}), represents the second one-electron transfer from L^- to an intermediate silver(II) species produced as a result of the first one-electron transfer and satisfies an $[OH^-]$-independent expression (ii). The k_f and k_s values are not influenced by the ionic strength (0.3—1.2

$$k_s = (1.46 \pm 0.02) \times 10^2[L^-]/\{1 + (56.0 \pm 3.5)[L^-]\} \qquad \text{(ii)}$$

mol dm^{-3}) of the medium nor by the presence of added pyrophosphate or silver(I) ions. Kinetic and spectral results are interpreted as suggesting that each of the processes mentioned most probably proceeds by a substitution-controlled mechanism at the silver centre.

We have been interested in the chemistry of the tetrahydroxoargentate(III) ion [1] and have studied its reactions with various reducing substrates (L).[2-11] The ion $[Ag(OH)_4]^-$ is a strong oxidant and typically accepts, stepwise or simultaneously, two electrons leading to the formation of a silver(I) species $\{Ag_2O$, $[Ag(OH)_2]^-$ and/or a complex of Ag^I with the excess of substrate used$\}$. The proportion of metallic silver, by the transfer of a third electron from an excess of L, is not discernible in many reactions and is very slow in others. For example, while the reaction of Ag^{III} with low excesses of ethylenediamine (en) finally produces silver metal,[2] that with HO_2^- gives products which are consistent with the observed stoicheiometries of both one- and two-electron change, with respect to the initial silver, per unit of the reducing substrate.[3] In oxygen-atom-transfer reactions of $H_nAsO_3^{(3-n)-}$ (where $n = 0$—2)[4] and SO_3^{2-},[5] the products are those which involve the consumption of 1 mol of Ag^{III} per mol of the reacted L. In the case of $S_2O_3^{2-}$ and N_3 each mol of Ag^{III} requires 2 mol of the reductant for the formation of the products.[6,7] With substitution-inert one-electron reductants,[8,9] the stoicheiometric ratios of $[Ag^{III}]:[L]$ are 1:2 for $[MnO_4]^{2-}$ and $[Fe(CN)_6]^{4-}$ and 1:1 for $[W(CN)_8]^{4-}$ and $[Mo(CN)_8]^{4-}$. Thus, in some reactions, the stepwise reduction of the Ag^{III} and the formation of the first one-electron transferred product Ag^{II} are apparent,[3,8,9] while in others [2,4-7] they are not individually detectable either because they are simultaneous or because one of the two steps is much faster than the other.

While there are no detectable Ag–L intermediates in the four reactions just mentioned, a number of other silver(III) redox reactions proceed by inner-sphere mechanisms through the formation of either a steady-state five-co-ordinate intermediate [2,3,10,11] involving an axial attack on square-planar silver(III) or of an identifiable, four-co-ordinate complex [6,7] involving ligand replacement.

Kinetics and mechanisms, as well as the final products, of the oxidation of simple monohydric phenols or their corresponding phenolate anions (L^- or PhO^-) are widely diverse and depend on many reaction parameters. For example, when one-electron oxidants are used, the reductant transfers one electron in the primary step to give the corresponding aryloxy radical [12] which rapidly dimerizes and/or rearranges to various products. Simultaneous two-electron transfer is common when the oxidant is a two-electron acceptor.[13,14] Exceptions, however, do occur for both of these categories.[12,15,16] Similarly, in some reactions of these reducing substrates, an outer-sphere electron-transfer mechanism is implicated,[17] while in others inner-sphere processes have been reported either through the interpretation of observed kinetic data or the identification of metal–phenolate intermediate complexes.[13-15]

In the light of the variety of possibilities, the present study of the kinetics of reduction of $[Ag(OH)_4]^-$ by 4-t-butylphenolate anion was undertaken with a view to understanding some of the mechanistic aspects, particularly pertaining to the chemistry of silver. It is hoped that the oxidation of this substrate will serve as a probe for delineating two stepwise one-electron *vs.* a simultaneous two-electron transfer from the Ag^{III}.

Experimental

Materials.—All the reagents used were of reagent grade. A colourless sample of 4-t-butylphenol (Eastman Kodak Co.) was recrystallized from ethanol and its solutions were freshly prepared before use by dissolving in alkali of appropriate strength. Solutions of $[Ag(OH)_4]^-$ were freshly prepared in 1.2 mol dm^{-3} NaOH by the electrolysis of a silver-foil anode and a silver-foil cathode, using a slight modification [10,11] of the procedure previously described.[1]

Kinetics.—The kinetics was studied by stopped-flow spectrophotometry as described previously.[6,7] The ionic strength of the medium was maintained by means of sodium perchlorate as the supporting electrolyte. In all runs, the initial concentration of the substrate was at least ten times higher than that of the disappearing Ag^{III}, the latter being in the range 0.5×10^{-4}—5×10^{-4} mol dm^{-3}. Silver(III) has a charge-transfer band at 267 nm {ε_{267} of $[Ag(OH)_4]^- = 1.17 \times 10^4$ dm^3 mol^{-1} cm^{-1} in aqueous alkaline solutions}[1b] and the deprotonated (pK_a = 10.2)[18] phenol has a maximum at 287 nm ($\varepsilon_{287} = 2.65 \times 10^3$ dm^3 mol^{-1} cm^{-1} for 4-t-butylphenolate anion in 1.2 mol dm^{-3} aqueous NaOH). The reaction product absorbs more strongly than either of the two reactants at wavelengths beyond 440 nm. The kinetics of the reaction was generally monitored as the disappearance of Ag^{III} at 330 nm where the absorbance of the substrate or the product was negligible (*cf.* ε of Ag^{III} is 1 800 and that of the substrate is 2 dm^3 mol^{-1} cm^{-1} at 330 nm). When the disappearance of Ag^{III} was monitored at other wavelengths in the 330—400 nm range, the observed rates were essentially identical. The kinetic data reported here are at 25 ± 0.1 °C and have a reproducibility within ±5%. U.v.-visible spectra were recorded on a Cary 15 spectrophotometer.

Products.—The stoicheiometry runs under the conditions of an excess Ag^{III} over the reductant could not be interpreted as the ratios were varying. For example, when $[Ag^{III}]_0$ was in the range 5×10^{-4}—2×10^{-3} mol dm^{-3} and $[L^-]_0$ was 1×10^{-4}—1×10^{-3} mol dm^{-3}, all the Ag^{III} reacted and the ratios of $\Delta[Ag^{III}]/\Delta[L^-]$ were different, lying in the range 2—10. Since phenol-oxidation products are often known to be variable, the observed results are not unexpected.

The following procedure was adopted to identify qualitatively the principal oxidation product, under a specified condition employing a slight excess of the oxidant over the phenol. In a total volume of 500 cm^3, a solution containing 4×10^{-3} mol dm^{-3} of Ag^{III} and 3×10^{-3} mol dm^{-3} of the phenol in 1.2 mol dm^{-3} NaOH was allowed to react to completion. The black precipitate of metallic silver was filtered using a medium-porosity glass sinter. The filtrate was neutralized with $HClO_4$ (pH ≈ 1) and then extracted repeatedly with diethyl ether. The aqueous layer was evaporated yielding a yellow solid which was thoroughly washed with large portions of water so as to wash down any unreacted and adhering phenol reactant. The remaining solid was extracted with dry ether, the ether layer separated, dried over anhydrous Na_2SO_4, and the ether evaporated in an ice-bath. The resulting solid was recrystallized from a minimum volume of hot methanol whence, after drying, deep yellow needles were obtained. The product was identified[19,20] as 2,2′-dihydroxy-5,5′-di-t-butylbiphenyl (**A**) from the i.r. spectrum. The important bands (cm^{-1}) were: 3 240 [br, ν(O–H)], 3 030, 3 000 [ν(C–H) aliphatic], 2 960 [$\nu_{asym}(CH_3)$], 2 865 [$\nu_{sym}(CH_3)$], 1 880 [overtone of ν(C–H) out-of-plane], 1 600, 1 510 (phenyl), 1 450 (overtone of aromatic), 1 380, 1 360 (doublet, phenolic O–H bend), 1 180 (C–OH phenol), 1 110, 1 010, 930 (t-butyl), 847, 825, 712, and 655 (1,2,4-substituted benzene nucleus).

Table 1. Pseudo-first-order rate constants for the two-stage reaction of 4-t-butylphenolate anion (L^-) with silver(III) at 25 °C and I = 1.2 mol dm^{-3}

$10^3[L^-]$	$[OH^-]$	k_f[a]	k_f(calc.)[c]	10^2k_s[b]	10^2k_s(calc.)[d]
mol dm^{-3}		s^{-1}		s^{-1}	
0.5	1.2	1.17	1.06	7.2	7.1
1.0	1.2	1.84	1.80	13.7	13.8
5.0	1.2	7.79	7.70	57.2	56.9
10	1.2	14.7	15.1	93.2	93.4
5.0	0.60	9.13	8.80	58.5	56.9
	0.30	11.8	11.0	56.7	56.9
	0.12	18.5	17.6	56.0	56.9
1.0	0.60	1.90	2.02	13.8	13.8
	0.30	2.14	2.46	13.5	13.8
	0.30	2.10[e]		13.0[e]	
	0.30	2.11[f]		13.7[f]	
	0.30	2.12[g]		14.1[g]	
	0.30	2.00[h]		14.3[h]	
	0.12	3.81	3.78	12.9	13.8

[a,b] Pertaining to the initial faster and second-stage slower absorbance decrease at 330 nm, respectively. [c,d] Calculated according to equation (3) [or (1)] and (4) [or (2)] respectively. [e,f] Respectively in the presence of 1×10^{-4} and 5×10^{-3} mol dm^{-3} of added $P_2O_7^{4-}$. [g,h] Respectively in the presence of 1×10^{-5} and 2×10^{-4} mol dm^{-3} of added Ag^I.

Results

When basic solutions of $[Ag(OH)_4]^-$ and the substrate phenolate anion are mixed in the stopped-flow assembly, under the conditions of $[L^-] > [Ag^{III}]$ and with monitoring below 400 nm, there is an initial, fast decrease in the absorbance, followed by a second-stage, slower absorbance decrease. The two stages of absorbance decrease are distinct, well separated, and each follows strict pseudo-first-order kinetics, the rate(s) being independent of the initial $[Ag^{III}]$ in the range 5×10^{-5}—5×10^{-4} mol dm^{-3}. The rates of absorbance decrease for both the stages are independent of the monitoring wavelength in the 330—400 nm region although the magnitude of the decrease is the greatest at 330 nm because of the higher extinction of the disappearing silver species and the minimum interference by the substrate and/or product solution. In terms of the actual absorbance decrease there is about 30% decrease in the initial absorbance for the first stage of the reaction and then again about 30% decrease in absorbance from the start of the second-stage reaction (which is the absorbance corresponding to the infinity of the first-stage reaction) to the end. After these reactions, a very slow absorbance increase (half-life > 1 h) occurs due to the precipitation of silver metal. For each stage of the reaction the pseudo-first-order nature of the absorbance decrease is found to be satisfied for about four half-lives. Fitting the absorbance and time data of either or both the phases by a linear plot of $[\Delta(\text{absorbance})]^{-1}$ *vs.* time was not successful showing that the absorbance decrease does not follow a pseudo-second-order pattern. No attempt was made to study the third-stage absorbance increase due to the slow precipitation of silver metal.

Table 1 lists the pseudo-first-order rate constants for the two stages of the reaction. The rate constants pertaining to the initial, faster absorbance decrease, k_f, were seen to depend both on $[L^-]$ and $[OH^-]$. Plots of k_f *vs.* $[L^-]$, for different $[OH^-]$, were linear giving a common intercept at *ca.* 0.4 s^{-1} while the gradients, when plotted against $[OH^-]^{-1}$, were linear with a significant intercept. The k_f data of Table 1 obey equation (1)

$$k_f = a + b_1[L^-] + b_2[L^-]/[OH^-] \qquad (1)$$

with the rate parameters: $a = 0.330 \pm 0.009$ s^{-1}, $b_1 = (1.26 \pm 0.09) \times 10^3$ dm^3 mol^{-1} s^{-1}, and $b_2 = (2.64 \pm 0.28) \times 10^2$ s^{-1}.

The pseudo-first-order rate constant pertaining to the second-stage, slower absorbance decrease, k_s, was found to be independent of $[OH^-]$ for the 10-fold range studied. The k_s values increased with increasing $[L^-]$, but the magnitude of the rate increase at higher relative $[L^-]$ became smaller. (Higher concentrations of the substrate than those shown in Table 1 could not be employed because of solubility constraints.) A plot of $1/k_s$ *vs.* $1/[L^-]$ was linear with a significant intercept and slope. A non-linear least-squares treatment of the k_s data according to equation (2) gave a good fit, where $c = (1.46 \pm 0.02) \times 10^2$ dm^3 mol^{-1} s^{-1} and $d = 56.0 \pm 3.5$ dm^3 mol^{-1}.

$$k_s = c[L^-]/(1 + d[L^-]) \qquad (2)$$

Both the rate constants k_f and k_s are independent of the ionic strength of the medium (Table 2). Different concentrations of $P_2O_7^{4-}$ and Ag^I were added to test for uncomplexed silver(III) and possible reversibility, but they resulted in no appreciable influence on the rate constants.

Table 2. Pseudo-first-order rate constants for the two-stage reaction of 4-t-butylphenolate anion $[L^-]$ with silver(III) at various ionic strength, 25 °C, and $[L^-] = 1.0 \times 10^{-3}$ mol dm^{-3}

$[OH^-]$	I	k_f	10^2k_s
mol dm^{-3}		s^{-1}	
0.30	1.2	2.14	13.8
	0.90	2.06	13.8
	0.75	2.05	14.5
	0.60	2.15	13.3
	0.30	2.14	13.5
0.60	1.2	1.90	13.6
	0.90	1.83	14.3
	0.75	1.95	14.0
	0.60	1.98	13.5

Discussion

The kinetic data can be interpreted in terms of the Scheme.

Application of steady-state approximations to the intermediates (**B**) and (**C**) yields the rate law (3) for the first-stage reaction. This has the same form as (1) where $k_1 = a$, $k_3K_2 = b_1$, and $k_5K_2K_4 = b_2$.

$$\frac{-d[Ag^{III}]/dt}{[Ag^{III}]} = k_f = k_1 + k_3K_2[L^-] + k_5K_2K_4[L^-]/[OH^-] \quad (3)$$

The second-stage absorbance decrease represented by Scheme (*b*) results in rate equation (4), where $K_6 = d$ and $k_7 = c/d = 2.6$ s^{-1} [*cf.* equation (2)].

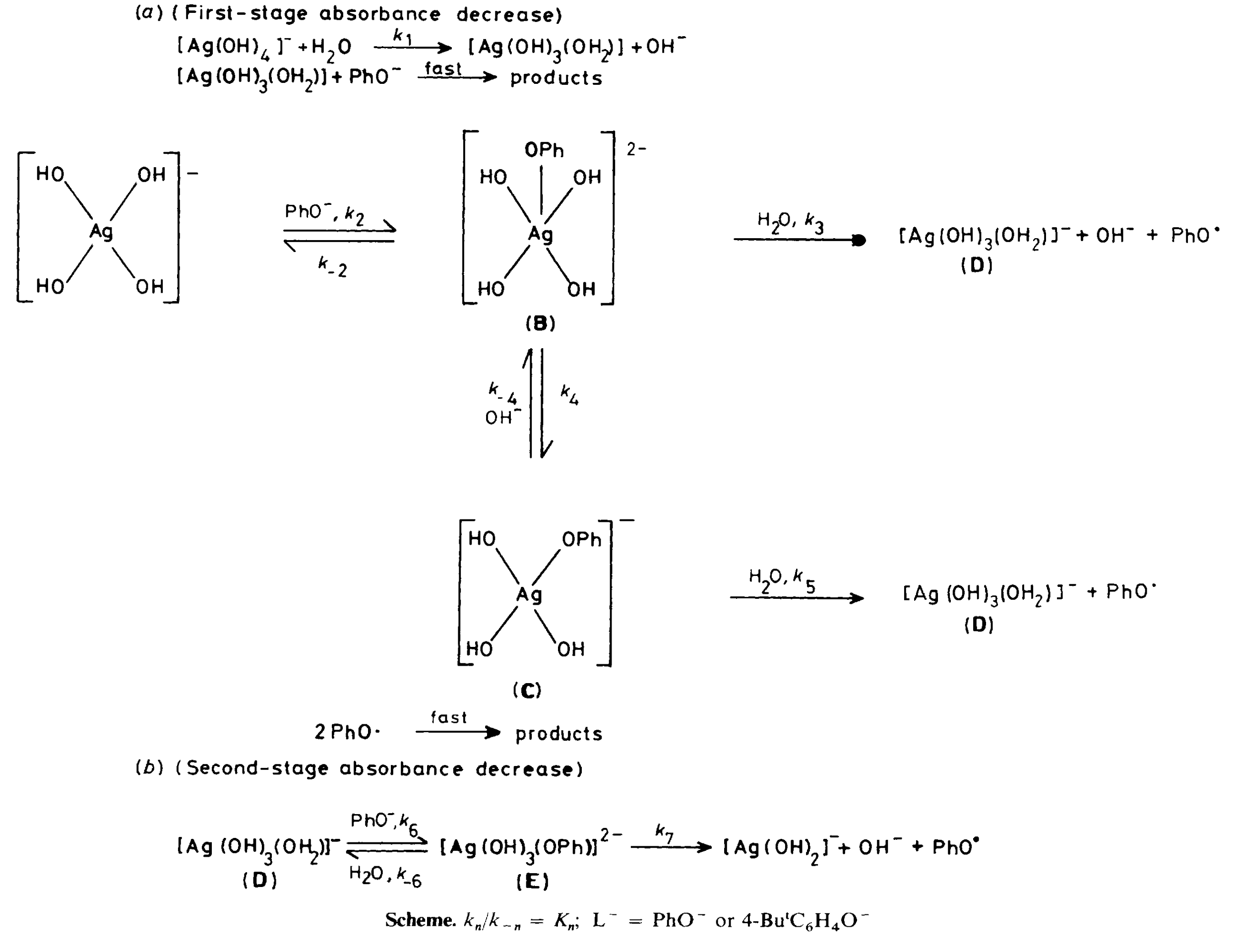
$$k_s = k_7K_6[L^-]/(1 + K_6[L^-]) \quad (4)$$

The very slow absorbance increase due to the precipitation of metallic silver is represented by a slow reduction of silver(I) product by PhO^- in alkaline solutions [equation (5)]. This was

$$[Ag(OH)_2]^- + PhO^- \longrightarrow Ag(s) + 2OH^- + PhO^{\bullet} \quad (5)$$

independently checked by starting with a similar concentration of $[Ag(OH)_2]^-$ as is expected to be produced from the original $[Ag(OH)_4]^-$ solution.

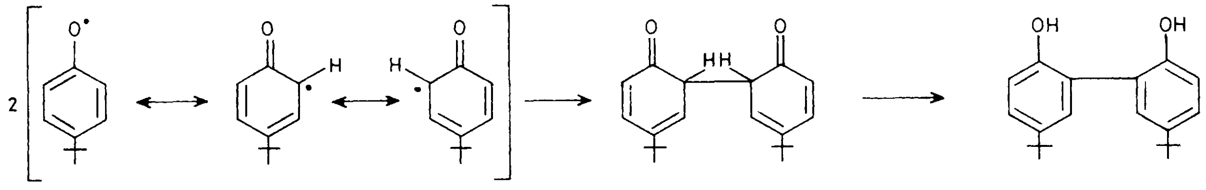
The kinetic observations of the present work appear to have several mechanistic implications. The first stage of absorbance decrease is obviously one corresponding to the disappearance of the initial silver(III) reactant as the exponential decay curve pertaining to this stage, when extrapolated to zero time, matches the initial absorbance of Ag^{III}. Moreover, no other absorbance changes are noticeable on the stopped-flow instrument (which has a dead time of 2 ms) prior to the first-stage absorbance decrease, suggesting that the first stage of silver(III) reduction is not preceded by any other faster reaction.



Scheme. $k_n/k_{-n} = K_n$; $L^- = PhO^-$ or 4-Bu^{t}C$_6$H$_4$O$^-$

The mechanism of the first-stage reduction of Ag^{III} (with the observed rate constant k_f) envisages that the PhO^- and the tetrahydroxoargentate(III) species, $[Ag(OH)_4]^-$, are involved in rapid equilibria forming an associative five-co-ordinate intermediate (**B**) and a four-co-ordinate intermediate (**C**) [with the replacement of a bound hydroxyl in the silver(III) species]. These precursor intermediates react with water with concomitant one-electron transfer, resulting in a silver(II) species (**D**) and a reactive phenoxy radical. The hydrolyzed silver(III) species, aquatrihydroxosilver(III), $[Ag(OH)_3(OH_2)]$, which is produced in a $[L^-]$-independent step, reacts very rapidly in kinetically indistinguishable steps so that the k_f value is limited by k_1 {*i.e.* the rate constant for the aquation of $[Ag(OH)_4]^-$} at very low concentrations of OH^- and L^-. It has been shown earlier[21] that the pK_a of $[Ag(OH)_3(OH_2)]$ is about 11 and k_1 has a value near unity.[2,3,5-7,11] The k_1 value of 0.33 s^{-1} calculated in this study is in reasonable agreement with previous estimates considering the fact that k_1 is not an independently measured value, but has been indirectly calculated from complex rate laws in different systems.

Aryloxy radicals, produced by a one-electron transfer, may undergo a variety of rapid reactions and, therefore, a variety of phenol-oxidation products may arise depending on the nature and reactivity of the substrate, the amount and oxidizing capacity of the oxidant, the presence of other reagents, and the reaction conditions employed.[22] The present product studies under the conditions described in the Experimental section indicate that the formation of the major product most probably involves a carbon–carbon coupling as shown in equation (6).



(6)

The intermediate aryloxy radical is sufficiently reactive (*viz.* the average lifetime of $PhO^{\bullet}$ is *ca.* 10^{-3} s[23] and that of $4\text{-}Bu^tC_6H_4O^{\bullet}$ with a *para*-substituted electron-releasing t-butyl group should be of the same order) and can react rapidly either by dimerization [equation (6), $k_{\text{dimerization}} = ca.\ 6 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$][24] or by electron transfer followed by an attack on another phenoxide.[25] Di- and poly-phenolic derivatives are often obtained as

$$PhO^{\bullet} \xrightarrow[\text{rapid}]{-e} PhO^+ \xrightarrow[\text{rapid}]{PhO^-} \xrightarrow[\text{rapid}]{} \text{products} \qquad (7)$$

the products of oxidation of phenols in alkaline solutions under conditions of a deficit of oxidant.[22] When the concentration of the oxidant, relative to that of the phenol, is higher, further oxidation of the polyphenols leads to quinone compounds.[13-17,22] Such complications are also possible in the present reaction and would account for the variable stoicheiometry under conditions of $[Ag^{III}]_0 > [L^-]_0$. However, the product formation steps are known to be very rapid and as such would not influence the kinetics of the reduction of silver species.

In the absence of other complexing agents, silver(III) exists only as the $[Ag(OH)_4]^-$ species in aqueous alkaline solutions as evidenced by a lack of spectral, kinetic, and stoicheiometry changes in a wide $[OH^-]$ range (*ca.* 0.1—12 mol dm^{-3}).[1] In the present study, therefore, the term in equation (1) containing $[OH^-]^{-1}$ cannot be traced to a speciation change in the initial reactant $[Ag(OH)_4]^-$.

The ion $[Ag(OH)_4]^-$ is a square planar system, and, like other low-spin d^8 metal ions, can either expand its co-ordination sphere or undergo ligand replacement.[26] The $[OH^-]$-independent and the $[OH^-]^{-1}$-dependent paths in equation (3) have been interpreted in terms of the formation of a five-co-ordinate (**B**) and a four-co-ordinate (**C**) precursor intermediate, respectively, the decomposition of which could be brought about by solvent water. The former situation has been realized earlier in several reactions of Ag^{III} with ethylenediamine,[2] HO_2^-,[3] and thiourea.[11] On the other hand, OH^- replacement has been observed in other reactions of Ag^{III}, where a $[OH^-]^{-1}$ dependence has been observed and a true four-co-ordinate complex spectrally characterized.[6,7] For example, in the case of the N_3^- reaction,[7] the apparent equilibrium constant for the replacement of one OH^- by N_3^- is 0.4. The spectrum of $[Ag(OH)_3(N_3)]^-$ is very similar to that of the original $[Ag(OH)_4]^-$ in the u.v. region (250—340 nm), but the azido complex has a small maximum at 410 nm. For the $S_2O_3^{2-}$ reaction,[6] an equilibrium constant of 1×10^4 was determined. The ion $[Ag(OH)_3(S_2O_3)]^{2-}$ has a spectrum similar to that of $[Ag(OH)_4]^-$ but with higher absorptions. Although a comparison of the point-by-point spectrum of the reaction mixture in the present case (320—400 nm, just after mixing) does not show any discernible absorbance change from those of the $[Ag(OH)_4]^-$ (see below), this negative observation is not inconsistent with transient complexes of similar absorbances and/or low equilibrium constant. The oxygen of phenolic hydroxyl is well known to be a potential donor in co-ordinating to metal centres, and a change in co-ordination from ^-OH to ^-OPh in Ag^{III} is not expected to bring about any spectacular spectral change. Therefore, we conclude that the first stage of reduction of Ag^{III} (represented by the observed rate constant k_f) most probably proceeds by the parallel paths shown in Scheme (*a*). The independence of k_f of ionic strength is not incompatible with this scheme.

One other alternative to Scheme (*a*) was also considered and discounted. It may be argued that the $[OH^-]$-independent and the $[OH^-]^{-1}$-dependent paths could arise from bimolecular interactions of $[Ag(OH)_4]^-$ with PhO^- and the neutral PhOH, respectively, according to equations (9) and (10). The rate

$$PhOH + OH^- \rightleftharpoons PhO^- + H_2O \qquad K_8 \approx 10^4\ (= K_a/K_w) \qquad (8)$$

$$[Ag(OH)_4]^- + PhO^- \longrightarrow [Ag(OH)_4]^{2-} + PhO^{\bullet} \qquad k_9 \qquad (9)$$

$$[Ag(OH)_4]^- + PhOH \longrightarrow [Ag(OH)_4]^{2-} + PhO^{\bullet} + H^+ \qquad k_{10} \qquad (10)$$

$$b_1 = k_9K_8[OH^-]/(1 + K_8[OH^-]) \approx k_9 \qquad (11a)$$

$$b_2/[OH^-] = k_{10}/(1 + K_8[OH^-]) \approx k_{10}/(K_8[OH^-]) \qquad (11b)$$

equation(s), (11a) and (11b), derived from this sequence identify $k_9 \approx b_1 = 1.26 \times 10^3\ dm^3\ mol^{-1}\ s^{-1}$ and $k_{10} \approx K_8b_2 = 2.64 \times 10^6\ dm^3\ mol^{-1}\ s^{-1}$ [*cf.* equations (1) and (2)] since $K_8[OH^-] \gg 1$.

It follows, then, that in the strongly basic solutions employed the less significant neutral PhOH species would be about three orders of magnitude more reactive than the predominant phenolate anion species PhO$^-$. Although this reactivity may outwardly appear to be following an electrostatic trend in the reaction of the negatively charged $[Ag(OH)_4]^-$, this is neither reasonable when one considers the nucleophilicity of the two substrate species attacking the central positive metal, nor consistent with electrochemical results in similar systems. For example, it has been well established[27] in studies on the electrochemical oxidation of a number of 2,4,6-substituted phenols in aqueous ethanol, acetonitrile, and other solvent media that the ease of oxidation decreases in the order: phenolate $\gg$ phenoxy radical $>$ phenol; this trend would predictably be maintained in an aqueous medium of higher dielectric constant. Therefore, it seems unreasonable that the neutral phenol species reacts several orders of magnitude faster than the predominant (and usually more reactive) phenolate anion. The redox potential for the couple 4-Bu^{t}C$_6$H$_4$O$^-$–4-Bu^{t}C$_6$H$_4$O$^•$ in aqueous alkaline solutions is not known, but if the reported redox potentials lying in the range *ca.* -0.2 to -0.3 V[27,28] for a variety of related couples 4-R-2,6-Bu$^t_2$C$_6$H$_2$O$^-$–4-R-2,6-Bu$^t_2$C$_6$H$_2$O$^•$ are any indication the present redox potential will not be widely different. The reactivities of the first electron-transfer step in the reaction of $[Ag(OH)_4]^-$ with $[Fe(CN)_6]^{4-}$, $[MnO_4]^{2-}$, $[W(CN)_8]^{4-}$, and $[Mo(CN)_8]^{4-}$ are well correlated to the redox potential,[8,9] while 4-t-butylphenolate reacts at a much slower rate than would be predicted. Although this comparison is very qualitative, it indicates that the present reaction [the first stage of silver(III) reduction] does not proceed by a single-step, bimolecular attack of the reductant species on the oxidant as suggested by equations (8)—(10).

It may be interesting to compare qualitatively the rates observed in the present studies with those reported for other $[Ag(OH)_4]^-$ systems. The second-order rate constants for the $[OH^-]$-independent term [k_3K_2 in equation (3)] are: en, 32.2;[2] tu, 1.46×10^3;[11] and PhO$^-$, 1.26×10^3 dm^3 mol^{-1} s^{-1} (this work). No simple parallelism appears to exist in these rates although the last two are similar. The rate constant of the $[OH^-]^{-1}$-dependent term, 2.64×10^2 s^{-1} for the PhO$^-$ reactant and 2.2×10^3 s^{-1} for $S_2O_3^{2-}$,[6] shows that $S_2O_3^{2-}$ is about one order of magnitude more effective than PhO$^-$ in bringing about the reduction of Ag^{III} through the four-coordinate intermediate.

The one-electron transferred intermediate (*i.e.* the aryloxy radical PhO$^•$) and the often-produced two-electron transferred intermediate (the aryloxonium cation PhO$^+$)[27,28] react at speeds which are near-diffusion controlled and, therefore, the second-phase absorbance decrease cannot be due to the reactions of these intermediate-oxidized forms of the substrate. The second stage has been assigned to the reaction of a silver(II) species with PhO$^-$. The rate constant for the second-stage absorbance decrease, k_s, is $[OH^-]$ independent, but linearly increases with $[PhO^-]$, showing a tendency to limiting values at high relative reductant concentration. The k_s (like the k_f) values are not influenced by the presence of added Ag^I, $P_2O_7^{4-}$ nor by changing the ionic strength of the medium. The kinetic rate law [equation (4)] nicely interprets the observed data, but the following details need discussion.

Point-by-point spectra, in the 330—580 nm region, of the reaction mixture (containing initially $[Ag^{III}] = 8 \times 10^{-5}$, $[PhO^-] = 5 \times 10^{-4}$, $[OH^-] = 0.3$ mol dm^{-3}, at 10 °C, $I = 1.2$ mol dm^{-3}) on the stopped-flow instrument at 2 ms, 1 s, and 10 s after mixing are presented in the Figure. As has been mentioned earlier, the absorbance 2 ms after mixing is the same as that due to the reactant(s), that after 1 s of mixing corresponds to a situation where the first phase of silver(III) reduction is over, and the absorbance after 10 s reasonably corresponds to that of the product(s) of the reaction (but before the precipitation of the silver metal has started). The spectral changes are small and contain a good deal of scatter due to unavoidable variations in initial [Ag^{III}], but the spectrum of the intermediate is discernibly different from that of the initial reactant(s) or the product(s). Moreover, stopped-flow traces of the reaction at different wavelengths (*a*) showed a biphasic absorbance decrease in the 330—400 nm region, (*b*) showed little change in the 410—430 nm range, and (*c*) displayed an absorbance increase followed by a slower absorbance decrease at higher wavelengths. The difference spectra [Figure (*b*)] indicate that (*i*) in the 330—400 nm range the solution of the intermediate has lower absorbances than the initial reactants (predominantly the Ag^{III} as the phenolate absorbs negligibly), (*ii*) in the 440—600 nm range the intermediate has higher absorbances than either that of the reactant or of the product solutions, and (*iii*) the reactants, products, and the intermediate have almost identical absorbances in the 410—430 nm region. The weak absorptivity of the intermediate(s) in the lower energy (440—600 nm) region suggests that it might be due to a *d–d* transition in a d^9 silver(II) species although it is difficult to assign the origin of the transition of an unstable intermediate species in the absence of any other supporting observations.

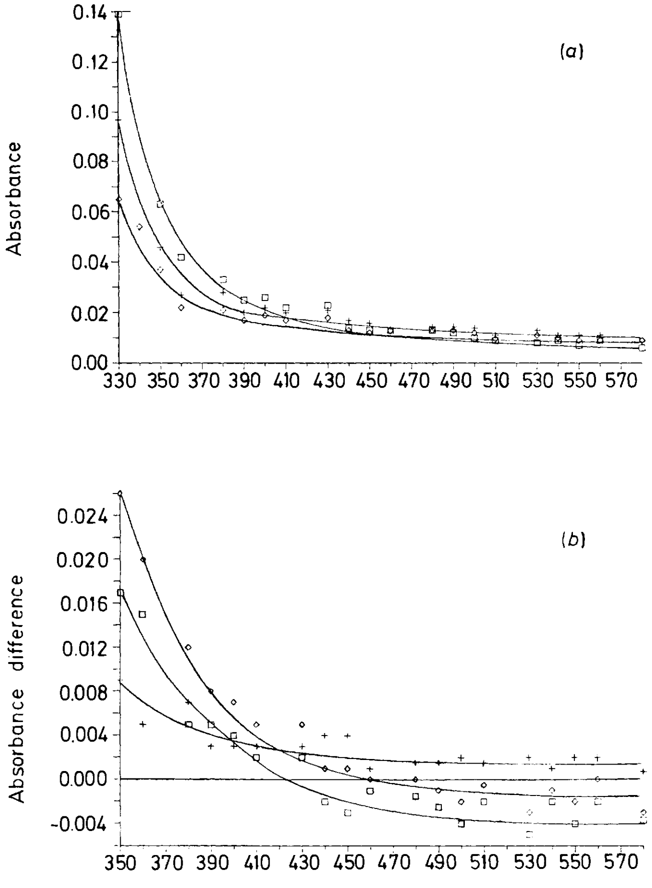


Figure. Visible spectra from stopped-flow wavelength variation. Conditions are given in the text. (*a*) Point-by-point spectrum at 2 ms (□), 1 s (+), and 10 s (◇) after mixing; (*b*) difference spectra corresponding to absorbance changes for (□) the first phase, (+) the second phase, and (◇) the overall reaction. Note, especially, the increase in absorbance (negative difference) for the first phase above 430 nm

The ion Ag^{2+} is metastable in acidic solutions, but no report is available on the spectral characteristics of uncomplexed silver(II) species in strongly alkaline media. We had attempted earlier to get spectral information on the silver(II) intermediate formed from $[Ag(OH)_4]^-$ in strongly alkaline solutions and noted that the apparent molar absorption of a dimerized silver(II) species is 4×10^3 dm^3 mol^{-1} cm^{-1} at 300 nm.[8,9] In a pulse-radiolysis study, it was found[29] that the dimerization rate constant of a silver(II) species, $Ag(OH)_2$, is near the diffusion-controlled limit (*ca.* 1×10^{10} dm^3 mol^{-1} s^{-1}) and the spectrum of $[Ag(OH)_2]_2$ has a significant absorptivity at 420 nm below pH 10 with the disproportionation of $[Ag(OH)_2]_2$ to Ag^I and Ag^{III} occurring within a few milliseconds. Rapid regeneration of trivalent silver does not appear possible under our experimental conditions since this would not lead to the observed biphasic kinetics. Moreover, the presence of added Ag^I does not alter the values of k_f and k_s showing that Ag^I is not involved in equilibria at any stage of the reaction. {The interaction of Ag^I with $[Ag(OH)_4]^-$ has been shown to be very slow.[3]} Pyrophosphate ion which brings about the one-electron reduction of Ag^{III} and stabilization of Ag^{II} at pH 6—8 (but not at pH > 9)[30] also does not have any influence on the two-stage kinetics (*cf.* Table 1). Therefore, it is reasonable to assume that under our conditions of observed pseudo-first-order kinetics for the two different and distinct phases, the Ag^{II} produced in the first-stage reduction of Ag^{III} undergoes electron transfer in the presence of an excess of reductant before any other complicated reaction involving itself discernibly occurs. Although Ag^{II} has been predicted to undergo substitution-controlled electron-transfer processes,[31] an unambiguous assignment of the actual silver(II) species in alkaline solutions as well as the silver(II)–substrate complex species is not yet possible.

Conclusions

The reduction of limiting tetrahydroxoargentate(III) ion by 4-t-butylphenolate anion follows two phases each exhibiting pseudo-first-order kinetics. The first, faster phase corresponds to one-electron transfer from the substrate to the initial reactant silver(III) species $[Ag(OH)_4]^-$. The second, slower phase represents a second one-electron transfer from the substrate to an intermediate silver(II) species produced as a result of the first one-electron transfer. These results suggest that each of the processes mentioned most probably follows a substitution-controlled mechanism at the silver centre.

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