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Kinetics of Oxidation of Aniline and Xylidines by the Tetrahydroxoargentate(III) Ion

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The reactions of $[Ag(OH)_4]^-$ with aniline and xylidines have been investigated. The stopped-flow experiments reveal kinetically distinguishable steps involving initial complexation of the substrate with the silver(III) species which is followed by its decomposition. The latter process obeys first-order kinetics and takes place with a rate constant of about 0.8 s^{-1} through intramolecular electron transfer from substrate to the silver(III) center. Azobenzene and *p*-benzoquinone have been identified as the main products of the reaction of $[Ag(OH)_4]^-$ and aniline. An increase in concentration of aniline enhances the yield of azobenzene which accounts for approximately 65% of the consumed aniline. This effect has been interpreted by the increased effective complexation between aniline and $[Ag(OH)_4]^-$ at higher concentrations. The stoichiometry of the reaction is found to vary with a change in the concentration of aniline. At higher concentrations it comes out to be 1 : 2 for $[Ag(OH)_4]^-$: aniline. A mechanism of this reaction is worked out.

The silver(III) species is known to be a powerful oxidant.[1,2] The reaction of Ag(III) with reducing substrates could not be investigated extensively in the past because of its transient nature.[3] The pulse radiolysis method, used for its generation, could not be exploited to carry out these reactions since the complexation and oxidation of the substrates occurred at shorter time scale by silver(II) species itself before they could disproportionate to produce Ag(III).[4] The study of these reactions could become possible by $[Ag(OH)_4]^-$ species which has been produced in a metastable state by the anodic oxidation of silver metal in the basic medium.[5] The reactions of some organics with $[Ag(OH)_4]^-$ have been investigated during last few years by Kirschenbaum and co-workers.[5c,6—11] From these investigations it is concluded that in general $[Ag(OH)_4]^-$ either undergoes substitution of OH^- with the substrate or forms a five-coordinate intermediate and then oxidation takes place by simultaneous two-electron transfer from the substrates to the silver center within this complex. In an exception, in case of 4-*t*-butylphenolate anion,[2] the oxidation is observed kinetically to take place stepwise through the formation of Ag(II) intermediate. It is curious that $[Ag(OH)_4]^-$ undergoes simultaneous two-electron as well as stepwise one-electron reduction. In view of this complex behavior, it is worth investigating the reactions of more organics with Ag(III) in order to elucidate the general mechanism.

In the present work, we report the oxidation of aniline and xylidines by $[Ag(OH)_4]^-$. Kinetics of these reactions and an enhancement in the yield of the product with increasing amines indicate the initial complexation between the substrate and the silver(III) species prior to their oxidation. Silver(III) and aniline reaction results in the formation of azobenzene and benzoquinone as the main products.

Experimental

Materials. Sodium hydroxide, diethylether, *p*-benzoquinone (Fluka/Merck), aniline, benzene (E. Merck, GR), azobenzene, *o*-aminophenol, *m*-aminophenol, *p*-aminophenol (Merck), acrylonitrile (SRL, AR), 2,4-, 3,4-, 2,6-dimethylaniline (Fluka), and silver foil (99.95% pure) were used. Aniline, dimethylanilines, aminophenols, azobenzene, and *p*-benzoquinone were purified by distillation/recrystallisation before use and their purity was checked by their electronic spectra and bp/mp. The analytical grade N_2/Ar, used for purging the OH^- solutions, were purified by passing them through Feiser's solution, pyrogallol in KOH and KOH solutions in order to remove any traces of O_2 and CO_2, respectively.

Equipments. The electronic spectra were recorded on a Shimadzu UV-vis-2100/s spectrophotometer. The gas chromatographic experiments were designed on a Hewlett Packard Model 5890A gas chromatograph equipped with integrator, F.I.D. detector, and split/splitless injector. GC-MS data were obtained on a Shimadzu QP-2000 instrument. Kinetics measurements were made on a 'Applied Photophysics' Model-1705 stopped-flow apparatus equipped with DL 905 datalab transient digitiser.

Methods. $[Ag(OH)_4]^-$ was generated electrochemically by the anodic oxidation of silver foil in 1.2 M NaOH (1 M=1 mol dm^{-3}) following the method developed by Kirschenbaum et al.[5b,5c] In a minor difference, we made use of an airtight borosil glass assembly for its preparation which had ports fitted with standard joints to hold the electrodes, an opening for flushing N_2 and an outlet. The $[Ag(OH)_4]^-$ thus formed had an identical electronic spectrum to that of reported by Kirschenbaum et al. It also formed a stable complex with periodate and a complex of intermediate stability with dimethylglyoxime as found earlier.[5b,10]

Thin layer chromatographic experiments were performed on silica gel plates using benzene as eluent.

The gas chromatographic separations were achieved on fused silica capillary column with crosslinked 100% dimethyl polysiloxane HP-1 (5 M×0.53 mm i.d. coated with 2.65 mm film thickness) under non-isothermal conditions. The following experimental conditions were maintained for these experiments—injector temperature 200 °C, detector temperature 220 °C and GC oven was temperature programmed from 40—180 °C at a heating rate of 10 °C min^{-1}. GC-MS experiments were performed at 70 eV and 250 °C using

ULBON HR-1 column (fused silica capillary-0.25 mm×50 m with film thickness-0.25 micron). The GC-MS data were recorded after the elution of the solvent.

All kinetics experiments were carried out under pseudokinetic conditions having excess of aniline at 20±1°C. Both the reactants were very well deaerated and filled in the driving syringes under Ar atmosphere.

Results and Discussion

Product Analysis. The reaction of aniline with silver(III) was carried out by adding it to the stock solution of $[Ag(OH)_4]^-$. It turned the solution dark yellow instantaneously which displayed several peaks at wavelengths 230, 270, and 420 nm, respectively. This absorption spectrum was found to change with time, it depicted an increase in the visible range with a simultaneous decrease in the UV region and had an isosbestic point at 343 nm. The solution remained quite clear for about 35 min and thereafter some black suspensions could be seen. This suspension could neither be dissolved in aqueous ammonia nor in dilute acid solution indicating it to be the silver metal. The products of this reaction could be extracted in diethylether. The black suspension which gets accumulated at the juncture of the two layers and on the wall of the vessel was separated out. The ether extract of the product at very low concentration of aniline, where most of the aniline is consumed, showed the electronic spectral features resembling fairly well with the mixture of authentic sample of azobenzene and *p*-benzoquinone. The formation of these products was verified qualitatively in TLC experiments using their authentic samples.

To further isolate and identify the different components, a gas chromatographic separation involving aniline and its various possible oxidation products viz., *p*-benzoquinone, *o*-, *m*-, *p*-aminophenols, and azobenzene was developed.[12] The ether extract of the product was subjected to GC analyses. Two components corresponding to the retention time of *p*-benzoquinone (1.16 min) and azobenzene (9.44 min) were identified. Their formation was further confirmed in GC-MS experiments. At higher concentration of aniline, azobenzene was found to be the only product with mass spectral fragmentation m/z 182 (p 27), 105 (25), 77 (B), and 51 (33). This spectrum was identical to the mass spectrum of the authentic sample of azobenzene and its previously reported spectrum.[13]

The effect of the concentration of aniline on the yield of products was also investigated. The data obtained are summarized in Table 1. An increase in aniline enhances the yield of azobenzene appreciably but does not affect the amount of *p*-benzoquinone very much. For aniline concentration $\geq 1\times10^{-3}$ M, azobenzene was found to be the main product. From the observed yield of the product approximately 65% of the consumed aniline can be accounted for at higher concentration of aniline. Although one would expect the quantitative conversion of aniline into the product at its low concentrations but in the absence of appreciable amount of aniline, silver(0) formed in the reaction possibly catalyses the decomposition of silver(III) species.[14] It was also confirmed by us in a blank experiment.

Stoichiometry. The stoichiometry of this reaction was determined using gas chromatography by measuring the consumed aniline. At all concentrations of aniline no free $[Ag(OH)_4]^-$ could be detected even after 2 to 3 min of the reaction. The mole ratio of Ag(III): aniline was found to vary with a change in concentration of aniline. At low concentration ($\leq 5\times10^{-4}$ M) it was 1 : 1 and changed to about 1 : 2 at higher concentrations ($>1\times10^{-3}$ M). These facts are also indicated by the varying amount of the different products formed with increasing aniline.

Effect of Acrylonitrile. To verify the formation of free radicals as intermediate, the free radical scavenger, acrylonitrile (5% aq solution) was added to the reaction mixture immediately following the addition of aniline. The reaction mixture remained transparent initially. The white turbidity became visibly apparent after few hours. In cases of 2,4-, 2,6-, 3,4-dimethylanilines and *N*,*N*-dimethylaniline, the time of appearance of white turbidity were noted to be 50, 65, 45, and 4 min, respectively. In the absence of acrylonitrile, no such turbidity could be detected. It indicates the occurrence of polymerisation of acrylonitrile which would have produced white polyacrylonitrile, by the scavenging of free radicals. It is also revealed by a significant decrease in the amount of the product formed (ca. 50 to 70%) in their presence.

Kinetic Analyses. The kinetics of the reaction of Ag(III) species with aromatic amines was monitored at 310 and 400 nm as the used amines do not have appreciable absorption at these wavelengths. Moreover, the expected transients species to be formed, anilino radical does have small absorption coefficient at 310 nm and has its $\lambda_{\max}$ at around 400 nm. It may thus allow one to follow the decay of silver(III) absorption at 310 nm along with the formation of intermediate if any at 400 nm. Few of the representative kinetic traces for silver(III) and aniline reaction recorded at 310 and 400 nm have been depicted in Fig. 1. The kinetics of this reaction is quite complex and consists of four steps. The first two steps could not be analysed completely being quite mixed up. The initial decrease in absorbance of $[Ag(OH)_4]^-$ is considered due to its mixing with aniline solution, which leads to the aquation of this species.

$$[Ag(OH)_4]^- + H_2O \rightleftharpoons [Ag(OH)_3(H_2O)] + OH^- \quad (1)$$

This process does not show any effect of the concentrations of the reactants. This may be interpreted assuming that either an induction period exists or interaction with solvent occurs as shown in Eq. 1. Induction period has earlier been shown in the reaction

Table 1. Effect of Concentration of Aniline on the Yield of Product; $[Ag(OH)_4]^- = 6.5\times10^{-5}$ M

$[\text{Aniline}]_i$ $\times10^3$ M	[Aniline] $\times10^3$ M Reacted	[Azobenzene] $\times10^3$ M	[p-Benzoquinone] $\times10^3$ M	% Conversion of aniline into products
0.05	0.028	0.0028	0.0035	32.5
0.10	0.032	0.0036	0.0042	35.6
0.20	0.050	0.0095	0.0042	46.4
0.45	0.064	0.0135	0.0045	49.2
2.0[a)]	0.28	0.0917	—	65.5

a) $[Ag(OH)_4]^- = 1.25\times10^{-4}$ M.

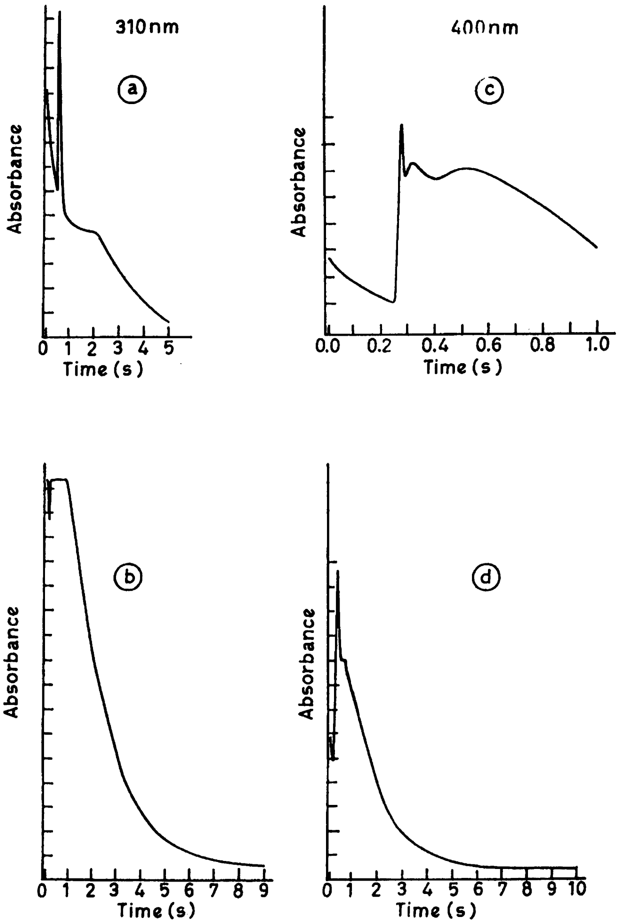


Fig. 1. Kinetic traces recorded at 310 (a and b) and 400 (c and d) nm for $[Ag(OH)_4]^-$ and aniline reaction containing $[Ag(OH)_4]^- = 1.25\times10^{-5}$ M, [Aniline] $= 5\times10^{-4}$ M and $[OH^-] = 0.6$ M.

of polypeptides with silver(III).[7)] Since the magnitude of decrease in absorbance is fairly large (ca. 40%) the possibility of this step being an induction period is thus ruled out in the present case. The aquation of $[Ag(OH)_4]^-$ species has previously been pointed out by Kirschenbaum et al. in the reactions of $[Ag(OH)_4]^-$ with ethylenediamine and thiosulfate ion.[6,8)] In their report rate of aquation is estimated to be (2±1) s^{-1} and this is indeed the time domain in which we have observed this process. The decreasing stability of $[Ag(OH)_4]^-$ with decreased $[OH^-]$ also suggests the involvement of water molecule in the decay of this species as shown in Eq. 1. The direct protonation rate for this process at low pH is though quite fast and has been estimated earlier to occur with a second-order rate constant of $\geq 5.5\times10^5$ $M^{-1}\,s^{-1}$.

The species $[Ag(OH)_3{\cdot}(H_2O)]$ is known to decompose in the basic solution to give solid silver oxide and oxygen.[8)] But in the presence of aniline it might have led to the formation of $[Ag(OH)_3(C_6H_5NH_2)]$ because of aniline being a better nucleophile than water and is seen as rapid build up in the kinetic traces.

$$[Ag(OH)_3{\cdot}H_2O] + C_6H_5NH_2 \longrightarrow [Ag(OH)_3(C_6H_5NH_2)] + H_2O \qquad (2)$$

This suggests that the reverse of reaction (1) is slow in comparison with the substitution reaction (2) despite of the previous being a proton transfer reaction. In basic medium the rate constant for the reverse of reaction (1) has been estimated to be much smaller (ca. 10^3 $M^{-1}\,s^{-1}$) than that of the diffusion controlled reaction.[8)] This decrease in deprotonation rate has been assigned to the hydrogen bonding in $[Ag(OH)_3{\cdot}(H_2O)]$ having proton possibly sandwiched between any of the two hydroxyl groups.

The intermediate $[Ag(OH)_3(C_6H_5NH_2)]$ shows higher relative absorbance than initial $[Ag(OH)_4]^-$ species and the magnitude of change in absorbance (ΔA) increases with increasing aniline in the concentration range of 2.5×10^{-4} to 1.5×10^{-3} M (Table 2). The ΔA approaches a limiting value above 1 mM of aniline. The saturation value is considered corresponding to the complete conversion of silver(III) into its uni(aniline) complex as shown in reaction (2). From these values of ΔA, an equilibrium constant for the above complex is estimated to be $(7\pm1.5)\times10^2$ M^{-1}. An increase in concentration of OH^- from 0.6 to 1.0 M did not affect the value of ΔA. It suggests that OH^- is not reversibly replaced in the formation of $[Ag(OH)_3(C_6H_5NH_2)]$. Thus the possibility of the following reaction is eliminated.

$$[Ag(OH)_4]^- + C_6H_5NH_2 \rightleftharpoons [Ag(OH)_3(C_6H_5NH_2)] + OH^- \qquad (3)$$

It indicates that under our experimental conditions,

Table 2. Equilibrium Constant of $[Ag(OH)_3(C_6H_5NH_2)]$; $[Ag(OH)_4]^- = 1.25 \times 10^{-5}$ M

[Aniline] $\times 10^3$ M	ΔA	$[Ag(OH)_3(C_6H_5NH_2)]$ $\times 10^6$ M	Equilibrium constant $\times 10^{-2}$ M^{-1}
0.25	0.0073	2.65	8.5
0.75	0.020	7.25	7.3
1.0	0.0238	8.62	6.9
1.25	0.0282	10.2	6.5
1.5	0.0306	11.1	5.9

rate for the formation of uni(aniline)silver(III) complex is essentially controlled by Eq. 1. We were, however, limited in increasing further $[OH]^-$ as it caused a decrease in the absorbance due to $[Ag(OH)_4]^-$ itself possibly because of its reaction with Na_2CO_3 which is present in trace amounts in our sodium hydroxide sample. Sodium carbonate is known to react with $[Ag(OH)_4]^-$.$^{5)}$ The species formed in Eq. 2 decays in the subsequent step. The rate for this process was found to depend on the concentration of aniline. An increase in concentration of aniline enhanced its rate proportionally and is assigned to the uptake of another ligand by uni(aniline)silver(III) complex.

$$[Ag(OH)_3(C_6H_5NH_2)] + C_6H_5NH_2 \rightleftharpoons [Ag(OH)_2(C_6H_5NH_2)_2]^+ + OH^- \qquad (4)$$

From the early part of these traces, a second-order rate constant for this step (Eq. 4) is computed to be $(5\pm2)\times10^3$ $M^{-1}s^{-1}$ (Fig. 2a).

Applying steady-state treatment to the two intermediates $[Ag(OH)_3(H_2O)]$ and $[Ag(OH)_3(C_6H_5NH_2)]$, the following rate expression for the complexation is obtained from the above proposed mechanism:

$$\frac{d}{dt}[Ag(OH)_2(C_6H_5NH_2)_2]^+ = \frac{k_1k_2[Ag(OH)_4]^-[C_6H_5NH_2]}{k_{-1}[OH^-] + k_2[C_6H_5NH_2]} \qquad (5)$$

Decomposition Kinetics. The above formed silver(III) complexes (Eqs. 2 and 4) disappear obeying first-order kinetics. The rate constant for this step decreased slightly with increasing aniline (1.3 to 0.8 s^{-1}) and attained a limiting value of about 0.8 s^{-1} above 1×10^{-3} M of aniline (Fig. 2b). This is attributed to the decomposition of the aniline silver(III) complex occurring through intramolecular electron transfer from aniline to the silver(III) center. A little higher rates at lower concentrations of aniline are understood by the decomposition of the mixture of uni- and bis(aniline)-silver(III) complexes (Eqs. 6 and 7) at these concentrations and apparently uni(aniline)silver(III) complex being having faster rate of decomposition. The formation of uni- and bis(aniline)silver(III) complex at low [aniline] ($<5\times10^{-4}$ M) and bis(aniline)silver(III) complex at higher [aniline] (>1 mM) is also consistent with the observed change in stoichiometry of the reaction from 1 to 2 by an increase in the concentration of aniline.

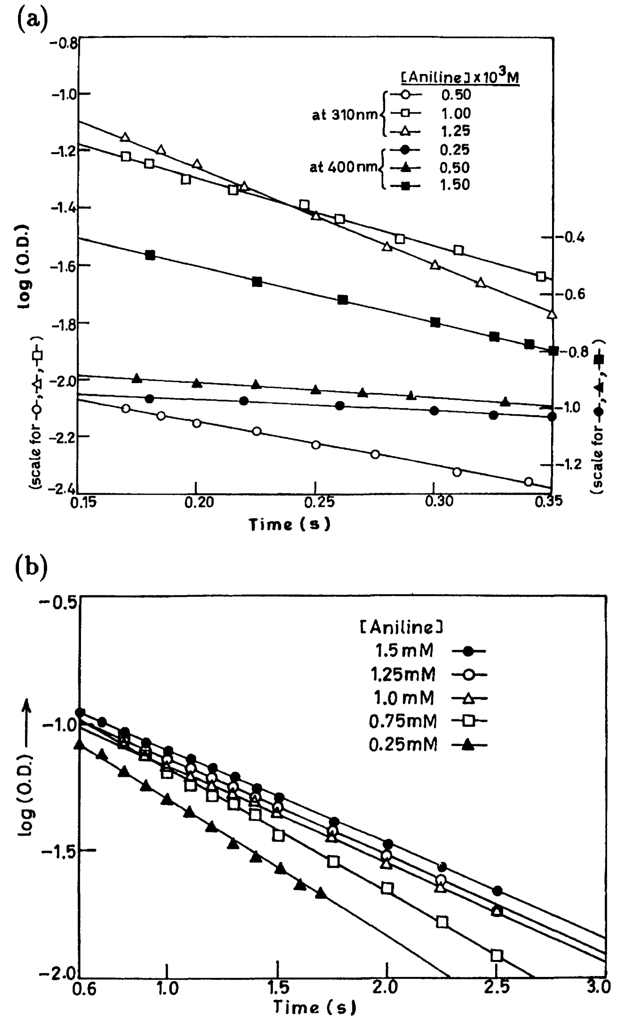


Fig. 2. (a) Effect of concentration of aniline on the formation kinetics of bis(aniline)silver(III) complex. (b) Effect of concentration of aniline on the decomposition kinetics of silver(III) complexes.

$$[Ag(OH)_3(C_6H_5NH_2)] \longrightarrow Ag(II) + C_6H_5\dot{N}H + 2OH^- + H_2O \qquad (6)$$

$$[Ag(OH)_2(C_6H_5NH_2)_2]^+ \longrightarrow Ag(I) + 2C_6H_5\dot{N}H + 2H_2O \qquad (7)$$

The rate for the reduction of silver(III) complex has been found to increase slightly with increasing OH^- concentration. An increase in OH^- from 0.6 to 1.0 M enhanced the rate constant from 0.8 to 0.9 s^{-1}. This supports the equilibrium shown in Eq. 4 and the hypothesis that uni(aniline)silver(III) complex decomposes at a faster rate. We rule out this change due to an increase in ionic strength since this reaction involves a neutral aniline molecule as one of the reactant.

Alternatively, one could argue the last two decay processes as the successive electron transfer reactions occurring through the formation of silver(II) intermediate. This possibility is, however, ruled out on the basis of pulse radiolysis data of Kumar and Neta[15] on silver(II) and aniline reaction. Silver(II) oxidises aniline with a rate constant of $(7.4\pm0.9)\times10^{8}\ \mathrm{M^{-1}\,s^{-1}}$ in the basic medium which is much faster than the above observed rate constant of $0.8\ \mathrm{s^{-1}}$.

$$\mathrm{Ag(OH)_2 + C_6H_5NH_2 \longrightarrow Ag(I) + C_6H_5\dot{N}H + OH^- + H_2O} \qquad (8)$$

Although a possibility that the reduction of silver(III) takes place by aniline in the slow step to produce silver(II) species which then oxidises aniline in the fast step cannot, however, be eliminated.

The kinetic behaviour at 400 nm was also very similar to that observed at 310 nm except that the second complexation step resulted in the formation of an intermediate which had a little higher absorption coefficient (Fig. 1c) and this absorption became more prominent at higher concentration of aniline. The latter decay process at this wavelength also obeys the first-order kinetics. Again the rate of this process was found to decrease with aniline and reaches a limiting value at approximately $0.8\ \mathrm{s^{-1}}$ (Fig. 1d). A similarity in kinetic behaviour at 310 and 400 nm clearly manifests that the decay at the two wavelengths is being caused by the same species. We did not detect any build up due to absorbing species like anilino radical at 400 nm following the latter decay which might have happened due to their recombination in the fast step. Anilino radicals are known to recombine rapidly with a second-order rate constant of $4\times10^{9}\ \mathrm{M^{-1}\,s^{-1}}$.[16]

The formation of an intermediate complex is also demonstrated by the increased yield of products at higher concentrations of aniline (Table 1) where efficient complexation between silver(III) and aniline is expected. Similar results on the product analyses were obtained for silver(II) and aniline reaction in which precomplexation between the two reactants was considered as the initial step. In these experiments also the radiation chemical yield was found to increase with increasing concentration of aniline.[15] Azobenzene was found to be the main product of this reaction.

The above identified products are apparently formed in two side reactions and can be conceived through stepwise one-electron oxidation of aniline which produces radical cation $\mathrm{C_6H_5\overset{\bullet+}{N}H_2}$.

$$\mathrm{[Ag(OH)_2(C_6H_5NH_2)_2]^+ \longrightarrow C_6H_5\overset{\bullet+}{N}H_2 + [Ag(OH)_2(C_6H_5NH_2)]} \qquad (9)$$

$$\mathrm{[Ag(OH)_2(C_6H_5NH_2)] \longrightarrow C_6H_5\overset{\bullet+}{N}H_2 + Ag(I) + 2OH^-} \qquad (10)$$

The radical cation $\mathrm{C_6H_5\overset{\bullet+}{N}H_2}$ has a pK of 7.[17]

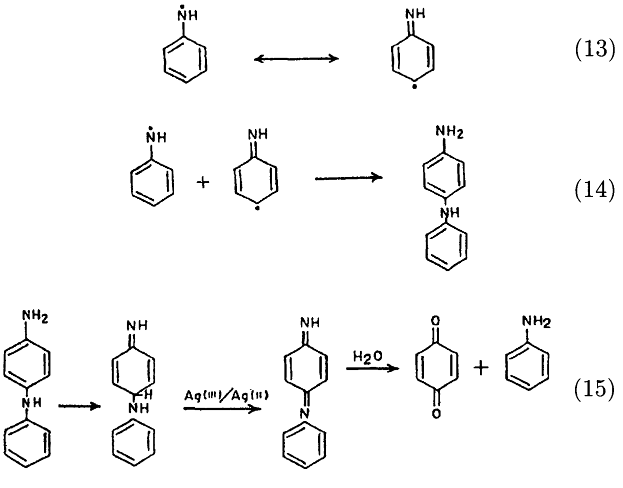
$$\mathrm{C_6H_5\overset{\bullet+}{N}H_2 + OH^- \longrightarrow C_6H_5\dot{N}H + H_2O} \qquad (11)$$

The hydrazobenzene is thus expected to be formed by the recombination of anilino radicals[16] which in the presence of Ag(I) gets oxidised to produce azobenzene. This process was found to obey first-order kinetics and occurs with a rate constant of $6.7\times10^{-4}\ \mathrm{s^{-1}}$ (Eq. 12). The occurrence of first-order kinetics suggests that silver(I) initially binds hydrazobenzene and then its oxidation takes place within the complex to produce silver(0) and azobenzene.

$$\begin{aligned}
&\mathrm{C_6H_5\dot{N}H + C_6H_5\dot{N}H \longrightarrow C_6H_5NH\text{-}NHC_6H_5}\\
&\mathrm{2Ag^+ + C_6H_5NH\text{-}NHC_6H_5}\\
&\qquad\mathrm{\longrightarrow [Ag(I)\ C_6H_5NH\text{-}NHC_6H_5\ Ag(I)]}\\
&\qquad\qquad\downarrow\\
&\qquad\mathrm{C_6H_5N{=}NC_6H_5 + 2Ag(0) + 2H^+}
\end{aligned} \qquad (12)$$

The oxidation of hydrazobenzene by Ag(I) to azobenzene was confirmed by us in a separate experiment. This transformation depicted an isosbestic point similar to that noted for Ag(III) and aniline reaction and also occurs on the same time scale.

The anilino radical may exist in another canonical form due to spin delocalisation and might undergo coupling to produce benzoquinone and aniline in the following mechanism:



Scheme 1.

At high concentration of aniline, N,N-recombination of anilino radicals to produce azobenzene apparently predominates over 4,N-coupling which yields benzoquinone. (Scheme 1)

To verify the above mechanism, we investigated the reactions of several other substituted anilines viz., 2,6-, 2,4-, and 3,4-dimethylaniline. The kinetic behavior of these reactions was very similar to that observed with $\mathrm{[Ag(OH)_4]^-}$ and aniline system. As expected the reaction of silver(III)-2,6-dimethylaniline results in the formation of 2,6-dimethyl-*p*-benzoquinone and 2,6,2′,6′-tetramethylazobenzene but in case of 2,4- and 3,4-dimethylaniline only one product, i.e., corresponding tetramethylazobenzene is formed. This is understood in terms of the blocking of the para position by methyl group in these substrates which prevents the formation of products as shown in Eq. 14.

The formation of azo-compounds have also been observed previously in the oxidation of aromatic amines by lead tetraacetate, and PbO_2.[18] These reactions are considered to involve the formation of free radicals as intermediates. In the present study, the products analyses and the effect of radical scavenging agent reveal the formation of anilino radical in the initial step. Moreover, the simultaneous two electron oxidation of aromatic amines would lead to the formation of phenylhydroxylamine type of product which has not been detected by us.

In summary, we have demonstrated that the oxidation of aniline by silver(III) involves an initial complexation to produce uni(aniline)silver(III) complex which uptakes another ligand to yield bis(aniline)silver(III) complex. Oxidation then takes place within the complex through stepwise electron transfer from substrate to the silver(III) center. Product analyses and effect of acrylonitrile demonstrates the occurrence of successive electron transfer although no kinetic evidence in its favor has been recorded. The fact that in certain cases one can distinguish kinetically two-electron transfer steps and in others not, appear to depend upon the lifetime of the transients and their further reactivity. The redox potential of Ag(III)/Ag(II) couple might also play an important role in demonstrating simultaneous or stepwise electron transfer. The substrates having lower oxidation potential than this couple would be expected to undergo stepwise electron transfer and that may be the case with the presently studied aromatic amines. A rough estimate of the redox potential of above 0.7 V has been made earlier for the couple $[Ag(OH)_4]^-/[Ag(OH)_4]^{2-}$. Successive one-electron transfer has been observed by Panda and Kirschenbaum in the reaction of silver(III) and 4-*t*-butylphenolate anion. The latter is expected to possess an oxidation potential similar to that of anilines.[19,20] The silver(II) species thus produced in the initial electron transfer process, might react either with the intermediate or substrate in the fast step. The latter possibility might be operative in the present system since Ag(II) is known to react with aniline and its derivatives readily.[15]

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