Complexation and Oxidation of Glycine and Related Compounds by Ag(II)[1]

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Abstract: The oxidation of glycine, several other amino acids, and carboxylic acids by Ag(II) has been studied. Transient spectra, kinetics, and product analysis indicate that the mechanism involves two steps. The first step is formation of a complex between Ag(II) and the substrate. The second step is an electron transfer from the carboxyl group to the Ag(II) within the complex. As a result, the substrate undergoes decarboxylation. The rate constants for complexation and oxidation were determined for a variety of substrates and with different forms of Ag(II), i.e., aquo, hydroxo, and ammino complexes. Both steps of the mechanism are affected by the structure of the substrate, for example, by the electron-donating properties of methyl groups and electron withdrawing by the NH_3^+ group. The rate of electron transfer within the complex is also affected by the structure and stability of the complex. The rate constants for complexation of the compounds studied under various conditions range from 10^6 to 10^8 M^{-1} s^{-1}. The rates of oxidation were usually of the order of 10^3 s^{-1}, although the highly stable complexes reacted more slowly.

Introduction

The reactions of bivalent silver ions with organic compounds have been the subject of numerous studies.[2-14] One of the reasons for the interest in these reactions is the attempt to elucidate the role of silver in the Ag^+-catalyzed oxidation of organic compounds by $S_2O_8^{2-}$.[2-9] It is generally accepted[8] that the initial reaction is

$$Ag^+ + S_2O_8^{2-} \rightarrow Ag^{2+} + SO_4^{2-} + \dot{SO}_4^- \quad (1)$$

followed by

$$\dot{SO}_4^- + Ag^+ \rightarrow SO_4^{2-} + Ag^{2+} \quad (2)$$

and the oxidation of the substrate by Ag^{2+}, e.g., with carboxylic acids

$$Ag^{2+} + RCH_2CO_2H \rightarrow Ag^+ + H^+ + RCH_2\dot{C}O_2 \rightarrow R\dot{C}H_2 + CO_2 \quad (3)$$

However, $\dot{SO}_4^-$ radicals may also react with the organic substrates, possibly to yield different intermediates, e.g., eq 4a,b. Therefore,

$$\dot{SO}_4^- + RCH_2CO_2H \rightarrow \begin{cases} R\dot{C}H_2 + CO_2 + H^+ + SO_4^{2-} & (4a) \\ R\dot{C}HCO_2H + H^+ + SO_4^{2-} & (4b) \end{cases}$$

the relative concentrations of Ag^+ and the organic substrate may affect the overall kinetics and products. The competition between reactions 2 and 4 can be predicted in many cases from known kinetic data. The rate constant for reaction 2 was previously estimated[8] as 3×10^9 M^{-1} s^{-1} and was measured in the present work to be $(4 \pm 0.5) \times 10^9$ M^{-1} s^{-1}.[15] The rate constants for reactions of $\dot{SO}_4^-$ with numerous organic compounds have been compiled[16] and the mechanisms discussed by several authors.[17] On the basis of the newly available kinetic data it can be shown that in many studies on Ag^+-$S_2O_8^{2-}$-RH systems the oxidation of RH took place by both Ag^{2+} and $\dot{SO}_4^-$. It is, therefore, imperative to study the reactions of Ag^{2+} separately.

The reactions of Ag^{2+} in the absence of peroxodisulfate have not been studied very extensively.[4b,10-14] Pelizzetti et al.[10,11] examined the oxidation of aliphatic carboxylic acids by Ag^{2+} in perchloric acid solutions. Trends in reactivities of these acids[11] were at variance with earlier findings[4a] by using the Ag^+-$S_2O_8^{2-}$ system. Walling and Camaioni[8] have recently explained this discrepancy in terms of solvent and pH effects. Reaction of $\dot{SO}_4^-$ with the acids could also contribute to the discrepancy. The effect of pH on the kinetics of Ag^{2+} reactions has in certain cases[11] been assigned to the equilibrium[18] $Ag^{2+} \rightleftarrows AgOH^+$, but on the basis of the recently determined[19] $pK_a = 5.35$, it can be concluded that this equilibrium is unimportant at the strong acidities used.[11] Instead, equilibria involving Ag(II) complexes with the organic acids[8] or with other anions[20] may have the major effect on the rates.

The present work deals with the oxidation of glycine and related compounds by Ag(II). It is concluded that complexation of the substrate with Ag(II) is the first step in all these oxidations.

(1) The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-2100 from the Notre Dame Radiation Laboratory.

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(15) This rate constant was measured by pulse radiolysis by following the kinetics of decay of $\dot{SO}_4^-$ as a function of Ag^+ concentration, as described earlier for other reactants; see, e.g., ref 17g. In irradiated solutions of Ag^+ and $S_2O_8^{2-}$ the decomposition of the peroxodisulfate takes place with $G = 3.7$, equivalent to the total yield of the reducing radicals, $G(e_{aq}^- + H)$, and indicating the absence of any chain reaction in this system.

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Experimental Section

The organic compounds used were purchased from Aldrich (glycine, α-aminoisobutyric acid, sodium nitrilotriacetate, *dl*-α-phenylglycine), Baker (benzaldehyde), Eastman (pivalic acid, *dl*-alanine, betaine), Fisher (ethylenediamine, formaldehyde), Matheson, Coleman and Bell (methylamine 40% solution), Cyclo (aspartic acid), and G. F. Smith (EDTA). The alcohols and the inorganic compounds were Baker Analyzed reagents except for silver perchlorate which was obtained from Alfa Chemicals.

Water was purified by a Millipore Milli-Q-system. Fresh solutions were prepared prior to irradiation, and the pH was adjusted using sodium hydroxide or perchloric acid. Oxygen was removed by bubbling with pure N_2 or N_2O. The N_2O serves as an electron scavenger which converts e_{aq}^- into OH efficiently ($N_2O + e_{aq}^- \rightarrow N_2 + OH^- + OH$).

Steady-state irradiations were carried out in a Gammacell 220 ^{60}Co source with a dose rate of 3.5×10^{17} eV g^{-1} min^{-1}. Pulse irradiations were carried out with 20-ns electron pulses from an ARCO LP-7 linear accelerator, supplying energy to produce 2–4 μM of radicals. Dosimetry was carried out by using N_2O-saturated KSCN solution. Further details of the techniques and the computer-controlled pulse radiolysis apparatus were given previously.[21]

For quantitative analysis of formaldehyde 4,5-dihydroxynaphthalene-2,7-disulfonic acid was used.[22] The product was monitored at 575 nm by using a Cary 219 spectrophotometer. Dilutions of a 37.4% w/w formaldehyde solution were used for calibration. Benzaldehyde was determined directly through its intense absorption at 249 nm ($\epsilon = 1.1 \times 10^4$ M^{-1} cm^{-1}).

Results and Discussion

Ag(II) was produced in irradiated aqueous solutions by the reaction of Ag^+ with OH radicals, which involves direct addition[19] or an inner-sphere electron transfer (see eq 5). This reaction is

$$Ag^+ + OH \rightarrow AgOH^+ \qquad (5)$$

followed by the acid–base equilibria (6).[19] All these Ag(II) species

$$Ag^{2+} \underset{pK_a = 5.35}{\rightleftharpoons} AgOH^+ \underset{pK_a = 8.35}{\rightleftharpoons} Ag(OH)_2 \qquad (6)$$

have absorption maxima near 300 nm. With the exception of Ag^{2+} in strongly acidic solutions,[11,20] the Ag(II) species decay within milliseconds to produce eventually Ag(I) and Ag(III).[23,24] Absolute rate constants for reactions of Ag(II) with organic substrates can be determined by monitoring the rate of decay of the Ag(II) absorption as a function of substrate concentration. Alternatively, the buildup of a substrate radical can be followed as reported previously, e.g., for alkoxybenzenes.[12,13] Rate constants for oxidation of the latter compounds by Ag^{2+} were in the range of 10^7–10^9 M^{-1} s^{-1}.[12,13] Reactions of Ag(II) with aliphatic compounds are expected to be slower and may be, therefore, difficult to measure by pulse radiolysis. The difficulty arises when, in order to compete with the second-order decay of Ag(II), the concentration of the substrate has to be increased to an extent that this substrate will compete with Ag^+ for the OH radicals and thus prevent the formation of Ag(II). This was found to be the case with *i*-PrOH and several other substrates where $k(Ag(II) + S)$ is estimated to be $<10^4$ M^{-1} s^{-1}.

While studying the reactions of Ag(II) with acids and especially with amino acids, one should take into account the complexation of these compounds with both Ag(I) ($K \approx 10^3$ M^{-1})[25] and Ag(II), with different coordination numbers and stability constants. In most experiments the concentrations were adjusted to allow most of the OH radicals to react with Ag(I) rather than with the organic substrate.[26]

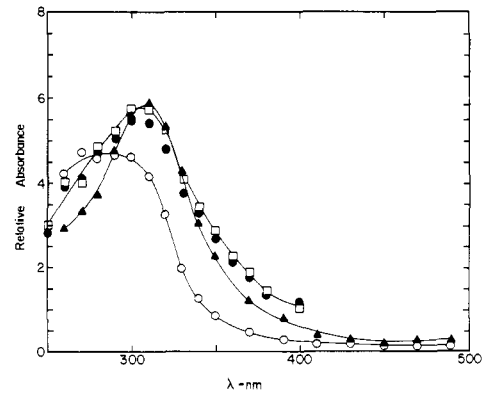

Figure 1. Transient absorption spectra observed with irradiated aqueous solutions of Ag^+ and glycine at pH 4.4. All solutions contained 1×10^{-3} M $AgClO_4$ and were saturated with N_2O: (▲) 1×10^{-3} M glycine, spectrum recorded 1 μs after the pulse; (○) 13 μs later; (□) 9×10^{-2} M glycine, 1 μs after the pulse; (●) 13 μs later. Each unit on the relative absorbance scale, in this and in the other figures, represents an extinction coefficient of 1000 M^{-1} cm^{-1} for a species produced with a yield of $G = 6$.

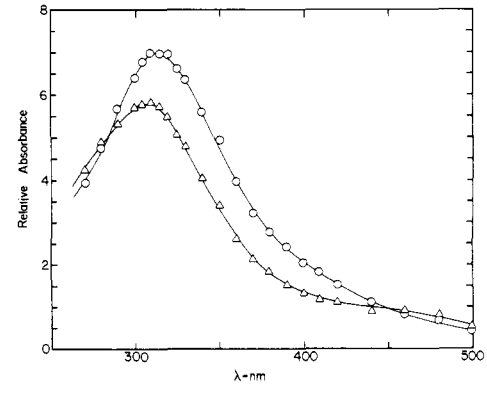

Figure 2. Transient absorption spectra observed with an irradiated aqueous solution of Ag^+ (1×10^{-3} M) and glycine (1×10^{-3} M) saturated with N_2O at pH 9.35: (△) recorded 2 μs after the pulse; (○) 30 μs later.

Glycine. Transient absorption spectra observed with irradiated solutions of Ag^+ and glycine under different conditions are presented in Figures 1 and 2. At pH 4.4 and 1×10^{-3} M glycine the spectra observed immediately after the pulse and 13 μs later (Figure 1) are identical with those observed for $AgOH^+$ and Ag^{2+}, respectively.[19,24] Under these conditions glycine does not compete with Ag^+ for OH radicals[26] and is not expected[25] to form a complex with Ag^+. The results indicate that it does not form a complex with Ag(II) either. However, when the concentration of glycine is increased to 9×10^{-2} M, complexation with Ag(II) takes place. This is apparent from the spectrum (Figure 1) which is different than that of uncomplexed Ag(II) and, furthermore, does not change with time.

At pH 9.35, glycine is ~30% in the basic form and is partly complexed with Ag^+. The transient spectrum (Figure 2) is somewhat similar to that observed at pH 4.4 with high [Gly] and can be assigned to $HOAg^{II}Gly$ formed by eq 7. This initial species

$$HO + Ag^{I}Gly \rightarrow HOAg^{II}Gly \qquad (7)$$

changes over 30 μs (Figure 2) into $Ag^{II}(Gly)_2$ produced by

$$HOAg^{II}Gly + Gly \rightarrow Ag^{II}(Gly)_2 \qquad (8)$$

in parallel with previous findings with ammonia.[23] The value of k_8 was measured from the kinetics of the spectral changes as a function of [Gly] (Figure 3). The first-order rate increases linearly with [Gly] and gives $k_8 = 6 \times 10^7$ M^{-1} s^{-1}. The slopes of the two lines determined at 330 and 400 nm (Figure 3) and of similar plots at 320 and 350 nm are similar within experimental error (±10%). However, their intercepts are different. The intercept observed at 400 nm indicates a reaction with a first-order

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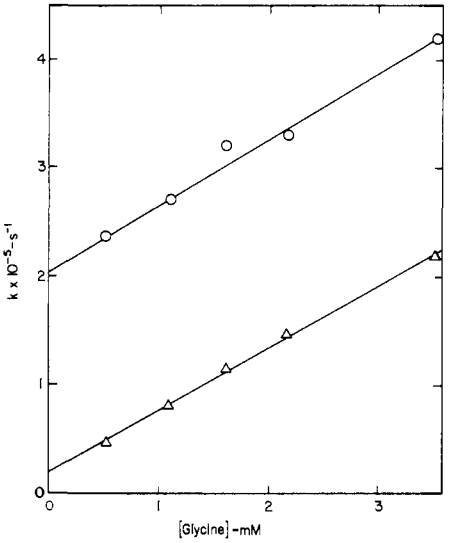


Figure 3. Effect of glycine concentration on the kinetics of spectral transformations at pH 9.0. All solutions contained 1×10^{-3} M $AgClO_4$ and were saturated with N_2O. The kinetics was monitored at 330 (△) and 400 (○) nm over a period of 20–50 μs following the rapid formation of the initial spectrum (see Figure 2).

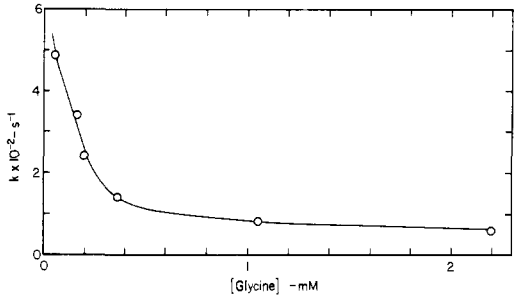


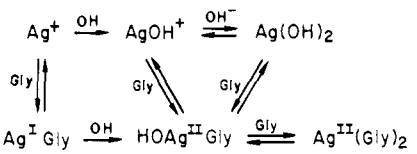
Figure 4. Effect of glycine concentration on the decay kinetics at pH 9.0. All solutions contained 1×10^{-3} M $AgClO_4$ and were saturated with N_2O. The kinetics was monitored at 310 nm over a period of ~10 ms.

rate of 2×10^5 s^{-1} independent of [Gly] which could be explained by eq 9[19] in competition with eq 10. The fact that at 330 nm

$$AgOH^+ + OH^- \rightarrow Ag(OH)_2 \quad (9)$$

$$AgOH^+ + Gly \rightarrow HOAg^{II}Gly \quad (10)$$

the intercept is very small indicates that a reaction with glycine is occurring which is independent of $AgOH^+$, i.e., reaction 8. The second-order rate constants for reactions 8 and 10 are experimentally indistinguishable, both $(6 \pm 1) \times 10^7$ M^{-1} s^{-1}. The observations in this system can be summarized in eq 11. The



(11)

final equilibrium between the various species in this scheme, achieved within ~100 μs, depends on the concentration of glycine. The decay of these species, observed over ~10 ms, follows a first-order behavior and is also found to be dependent on [Gly] (Figure 4). At low [Gly] ((0.5–3) $\times 10^{-4}$ M) the decay rate sharply decreases upon increasing [Gly] and then levels off at $k \approx 50$ s^{-1}. This plateau value probably represents the decay of $Ag^{II}(Gly)_2$ alone, while the higher rates are for mixtures of this species with others in eq 11. A similar trend was reported earlier for the system of Cu–Gly.[27]

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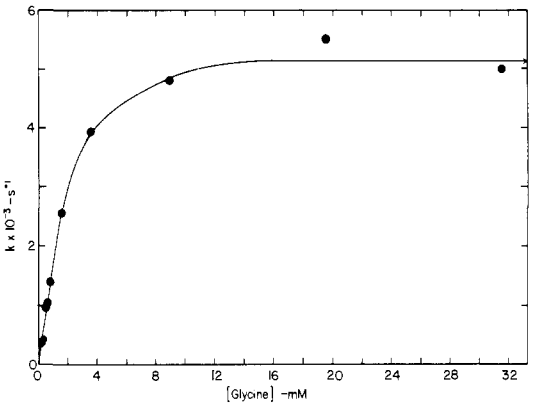

Figure 5. Effect of glycine concentration on the decay kinetics at pH 4.4. All solutions contained 1×10^{-4} M $AgClO_4$ and were saturated with N_2O. The kinetics was monitored at 310 nm over a period of 1–10 ms. An additional experimental point not shown in the figure is $k = 5.1 \times 10^3$ s^{-1} at [glycine] = 61 mM.

The absorption of $Ag^{II}(Gly)_2$ decayed to zero at the whole wavelength region (260–500 nm). A major product of this decay is formaldehyde (vide infra), indicating that glycine is oxidized by Ag(II) by an electron-transfer mechanism followed by decarboxylation. All the above findings suggest that this oxidation takes place within the complex and is faster in $HOAg^{II}Gly$ than in $Ag^{II}(Gly)_2$

$$Ag^{II}(Gly)_2 \rightarrow Ag^{I}Gly + H_2NCH_2C\dot{O}_2 \text{ (or } GlyAg^{I}H_2NCH_2C\dot{O}_2) \quad (12)$$

$$H_2NCH_2C\dot{O}_2 \rightarrow H_2N\dot{C}H_2 + CO_2 \quad (13)$$

$$2H_2N\dot{C}H_2 \rightarrow H_2NCH_2CH_2NH_2 \quad (14a)$$

$$2H_2N\dot{C}H_2 \rightarrow CH_3NH_2 + CH_2{=}NH \quad (14b)$$

$$CH_2{=}NH + H_2O \rightarrow CH_2O + NH_3 \quad (15)$$

The effect of [Gly] on the decay of the 310-nm absorption in acid solutions (Figure 5) was found to be in the opposite direction from that in the basic region. At [Gly] $\leq 2 \times 10^{-3}$ M the rate of decay increases linearly with [Gly] to give a second-order rate constant of 1.5×10^6 M^{-1} s^{-1}. Above 10^{-2} M the decay rate reaches a plateau at $(5.2 \pm 0.5) \times 10^3$ s^{-1}. This behavior indicates that at the higher concentrations, where Ag(II) is mostly complexed, the decay is an intramolecular electron transfer

$$HOAg^{II}Gly \rightarrow OH^- + Ag^+ + H_2NCH_2C\dot{O}_2 \quad (16)$$

At lower [Gly] the rate-determining step in the decay is the formation of the complex by reactions 10 and 17. The rate

$$Ag^{2+} + Gly \rightarrow Ag^{II}Gly \quad (17)$$

constant for this complex formation is 1.5×10^6 M^{-1} s^{-1} at pH 4.4, much lower than the value of 6×10^7 M^{-1} s^{-1} found at pH 9.0. At pH 4.4 the rate of complexation of glycine may be determined by interaction with the carboxyl group, while at pH 9 the glycine coordinates more rapidly through the amino group. By extrapolation, the rate constant for the fully basic form is evaluated to be 3×10^8 M^{-1} s^{-1}, over 2 orders of magnitude faster than that for the zwitterion.

While at pH 9.4 (Figure 2) the spectral changes are assigned to conversion of $HOAg^{II}Gly$ into $Ag^{II}(Gly)_2$, the spectra at pH 4.4 (Figure 1) are of mixtures of $Ag^{II}Gly$ and $HOAg^{II}Gly$ without reaching the more stable diglycine complex. This difference also accounts for the different kinetic behavior. While at pH 9.4 $Ag^{II}(Gly)_2$ formed at high [Gly] decays very slowly, the complexes formed at pH 4.4 are less stable and decay more rapidly.

α-Aminoisobutyric Acid (AIB). The results obtained with this compound are very similar to those with glycine. The effect of [AIB] on the kinetics, examined under identical conditions as those used with glycine (Figure 5), was found to be similar. The increase

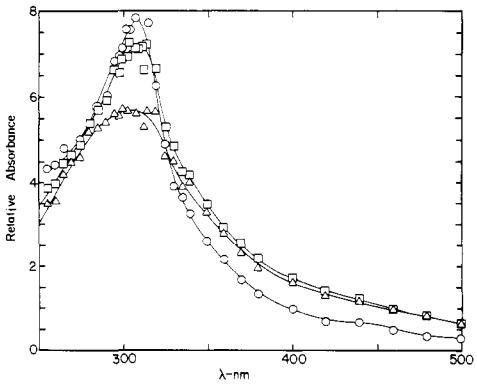

Figure 6. Transient absorption spectra observed with irradiated aqueous solutions of Ag^+ (5×10^{-4} M) and α-aminoisobutyric acid (5×10^{-4} M) at pH 9.6, saturated with N_2O: (△) monitored 5–6 μs after the pulse; (□) 25 μs later; (○) 80 μs later.

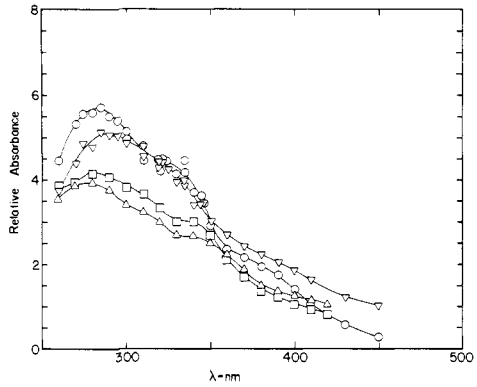

Figure 7. Transient absorption spectra observed with irradiated aqueous solutions of Ag^+ containing either EDTA or NTA. All solutions contained 1×10^{-3} M Ag^+ and were saturated with N_2O: (▽) 1×10^{-3} M NTA, pH 10.7, 1 μs after the pulse; (○) 12 μs later. (△) 1.2×10^{-3} M EDTA, pH 11.0, 2 μs after the pulse; (□) 12 μs later.

in rate with increasing [AIB] (5×10^{-5}–1×10^{-3} M) gives $k = 1.7 \times 10^6$ M^{-1} s^{-1} for the complexation of Ag^{2+} with AIB. At (2–10) $\times 10^{-3}$ M the rate remained constant at 5×10^3 s^{-1} assigned to the oxidation of the substrate within the complex.

The spectra observed at pH 9.6 (Figure 6) also change with time, due to further complexation of AIB with Ag(II). The spectra represent mixtures of $AgOH^+$, $HOAg^{II}AIB$, and $Ag^{II}(AIB)_2$ as discussed above. The rates of complexation and oxidation in the alkaline region were evaluated from the kinetics at 310 and 340 nm by using 7×10^{-5}–7×10^{-3} M AIB at pH 8.8. At lower [AIB] fast decay at 340 nm was observed due to reaction 9. In the millimolar range a buildup at 310 and 340 nm was observed, which gives a second-order rate constant of $(4 \pm 1) \times 10^7$ M^{-1} s^{-1}, assigned to the complexation process (eq 11). Following these initial rapid equilibria, the absorption decayed over the whole concentration range with a rate of $(4 \pm 1.5) \times 10^3$ s^{-1}, assigned to the oxidation of AIB by Ag(II) within the complex. This value is higher than that of glycine at pH 9 and in contrast with Figure 4 does not decrease with concentration. This dissimilarity may be the result of the electron-donating effect of the methyl groups, which facilitates oxidation of the carboxyl. The findings that oxidation of AIB is at least as fast as that of glycine at both pHs studied lend further support to the electron-transfer mechanism.

NTA and EDTA. The initial spectra observed with irradiated solutions of nitrilotriacetate (NTA) and EDTA containing Ag^+ (Figure 7) indicate the presence of complexed Ag(II). These species changed over 10 μs to yield more stable complexes. The spectral changes are not sufficiently large to allow detailed kinetic measurements. The process in these cases may be intramolecular, i.e., replacement of an OH group on the Ag(II) by a carboxyl group of the ligand already bound to the metal (eq 18).

$$OH + Ag^{I}NTA \rightarrow HOAg^{II}NTA \rightarrow Ag^{II}NTA \quad (18)$$

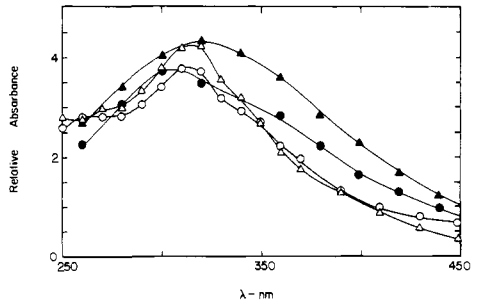

Figure 8. Transient absorption spectra observed with irradiated aqueous solutions of Ag^+ and pivalic or succinic acid. Pivalic acid, 9×10^{-4} M with 5×10^{-4} M Ag^+ at pH 4.3: (△) 1 μs after the pulse; (○) 5 μs later. Succinic acid, 1×10^{-3} M with 1.1×10^{-3} M Ag^+ at pH 5.6: (▲) 3 μs after the pulse; (●) 50 μs later.

The $Ag^{II}NTA$ complex decays by a first-order reaction with $k = (2 \pm 0.5) \times 10^3$ s^{-1} when [NTA] ≥ 1 mM. The decay at 300 nm appeared slightly faster at lower [NTA] where the Ag(II) is not fully complexed. $Ag^{II}EDTA$ also decays by a first-order reaction, but more slowly, $k = 8 \pm 2$ s^{-1} at [EDTA] = 0.5–3 mM.

Pivalic and Succinic Acids. The oxidation of pivalic acid by Ag(II) in strong acid takes place with a rate constant of 1×10^3 M^{-1} s^{-1} [11] but is expected to be faster in neutral solutions. Pivalic acid was, therefore, studied in order to examine this expectation and to compare its behavior with that of the amino acids. The spectra recorded at pH 4.3 indicate the formation of $Ag^{II}(piv)_n$ (Figure 8 and other spectra not shown). The decay of the 310-nm absorption was first order, with $k = (1 \pm 0.2) \times 10^4$ s^{-1} independent of [piv] from 2×10^{-4} to 1×10^{-2} M. This rate is assigned to the oxidation of pivalic acid within the $Ag^{II}(piv)_n$ complex. Below 1×10^{-4} M the rate was slightly lower, indicating the complexation to be the rate-determining step. It was not possible to determine the rate constant for the complexation over a wide range of [piv]. However, from the two lowest concentrations studied, the rate constant is estimated at $\sim 1 \times 10^8$ M^{-1} s^{-1}.

The spectra at pH 8.8 in the presence of 1×10^{-3} M pivalic acid were identical with those in its absence, and their time profile was also similar, indicating the lack of complexation and oxidation at this pH. This is not in contradiction with the rapid complexation observed in acid solutions, since under the latter conditions the Ag(II) is present as the aquo complex, which may be attacked by the pivalic acid more readily than the hydroxo complex. Differences between pivalate ion and pivalic acid in rate of complexation may also contribute to the above results.

Succinic acid showed a generally similar behavior. The spectrum at pH 5.6 had a broad maximum at 310 nm and slightly varied with time (Figure 8) presumably to produce a more stable complex. The rate for this process was difficult to measure because the spectral changes are small. The decay of the complex followed first-order kinetics with a rate of 2.0×10^2 s^{-1} at [succinic acid] = (1–4) $\times 10^{-4}$ M. This decay is slower than that observed with pivalic acid probably because the methyl groups in pivalic facilitate oxidation and, furthermore, the two carboxyl groups in succinic acid stabilize the complex.

Oxidation Products from the Amino Acids. Formaldehyde was found to be the main product of oxidation of glycine, NTA, and EDTA. Its formation indicates one-electron oxidation of these acids at the carboxyl group, followed by decarboxylation (reactions 12 and 13) as discussed previously.[28] The aminoalkyl radicals produced undergo reactions 14–15 to yield a carbonyl compound.[29] The yield of formaldehyde from the reaction of OH with glycine (Table I) is low

$$OH + H_2NCH_2CO_2^- \rightarrow H_2N\dot{C}HCO_2^- + H_2O \quad (19)$$

in agreement with that reported and discussed previously.[29] In

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Table I. The Yield of Formaldehyde in Irradiated N_2O-Saturated Solutions of Ag^+ with Amino Acids

substrate	[substrate], M	[Ag^+], M	pH	G-(CH_2O)[a]
glycine	5.5×10^{-3}	0	5.6	0.4
glycine	9.0×10^{-2}	1.0×10^{-3}	5.6	1.1
glycine	7.0×10^{-4}	5.6×10^{-4}	5.5	2.6
glycine	1.0×10^{-2}	1.0×10^{-3}	5.5	2.8
glycine	2.7×10^{-4}	5.4×10^{-4}	5.5	3.1
glycine	5.0×10^{-3}	0	8.9	1.0
glycine	7.0×10^{-4}	4.7×10^{-4}	8.9	1.8
glycine	5.1×10^{-3}	1.2×10^{-4}	8.9	1.8
glycine	6.1×10^{-3}	0	11.1	0.9
methylamine	5×10^{-2}	0	5.5	0.6
methylamine	5×10^{-2}	4×10^{-4}	6.0	2.6
methylamine	5×10^{-2}	1×10^{-3}	5.5	3.0
methylamine	5×10^{-2}	3.4×10^{-3}	5.3	3.6
NTA	3.4×10^{-4}	1.3×10^{-3}	9.0	5.8
NTA	5.9×10^{-4}	0	5	0.2
EDTA	3.0×10^{-4}	1.1×10^{-3}	9.1	6.0
EDTA	4.2×10^{-3}	0	5.3	0.6
EDTA	3.4×10^{-4}	1.1×10^{-3}	5.6	3.9

[a] G values are estimated to be accurate to ±0.1.

the presence of Ag^+ the yield of formaldehyde increases, indicating decarboxylation of glycine by Ag(II) (reactions 12–15). The yields vary greatly with concentration and pH, since several reactions take place in parallel and lead partially to CH_2O production.

The $\dot{C}H_2NH_2$ radical produced by decarboxylation of glycine undergoes reactions 14 and 15. The fraction of radicals which yield formaldehyde is estimated by producing $\dot{C}H_2NH_2$ quantitatively ($G = 6$) from $CH_3NH_2 + OH$. $G(CH_2O) = 0.6$ found in this case (Table I) indicates that reactions 14a,b take place with a probability of 4:1, respectively. However, in the presence of Ag^+ the radicals may be oxidized by Ag^+ to yield CH_2O quantitatively.

$$H_2N\dot{C}H_2 + Ag^+ \rightarrow CH_2{=}NH + H^+ + Ag^0 \qquad (20)$$

$G(CH_2O) \approx 3$ observed with methylamine and Ag^+ at pH 5.5 indicates that nearly 50% of the $\dot{C}H_2NH_2$ radicals are oxidized in this system. Radicals of this type are not oxidized by Ag^+ directly by a simple electron-transfer mechanism since this is thermodynamically impossible.[30] However, a series of complex reactions may lead to the same final result.[30] In the present work rapid oxidation of $H_2N\dot{C}HCO_2^-$ by Ag^+ is observed in the pulse radiolysis. Since the oxidation of $\dot{C}H_2NH_2$ by Ag^+ occurs with ~50% efficiency, if the oxidation of glycine by Ag(II) is quantitative, one would expect a yield of formaldehyde of $G = 3$. This value is indeed observed under certain conditions (Table I). The lower yields found at the relatively higher glycine concentrations are due to attack of OH directly on the glycine. At the high pH experimental limitations did not permit optimal conditions to reach $G = 3$.

In contrast with glycine, $G(CH_2O) = 6$ from NTA and EDTA in the presence of Ag^+ indicates quantitative oxidation of the ligand by Ag(II) followed by quantitative oxidation of the resulting radical by Ag(I). These processes are apparently efficient with NTA and EDTA because these ligands are multidentates and form stable complexes in which the radical produced by the first oxidation step remains bound to the Ag(I) and is efficiently oxidized by it. Ag^0 was also observed as a major product in these cases (in the form of a complex with intense absorption at 410 nm).

Oxidation of α-phenylglycine by Ag(II) yields benzaldehyde with $G = 5.8$. This value suggests that both oxidation steps discussed above are efficient. Oxidation by Ag(II) may take place through the carboxyl group as in the other amino acids and possibly through the phenyl ring as well. The latter route produces the cation radical which is also expected to undergo decarboxylation.[17] The resulting $C_6H_5\dot{C}HNH_2$ is further oxidized by Ag(I) to the imine, which then hydrolyzes to benzaldehyde. The second oxidation step is more efficient here than with glycine because of increased stability of the aromatic species $C_6H_5C^+HNH_2$ or $C_6H_5CH{=}NH$.

Oxidation by $Ag(NH_3)_4^{2+}$. All the oxidations by aquo Ag(II) ions discussed above were found to take place via an intramolecular mechanism following the binding of the substrate to the Ag(II). In order to examine the possibility of an outer-sphere electron-transfer mechanism, we used the more stable complex ion $Ag(NH_3)_4^{2+}$. The results in this case indicate, however, that binding of the substrate to the Ag(II) must precede the oxidation. Experiments were carried out with glycine, α-alanine, α-aminoisobutyric acid, and aspartic acid by using 1 mM Ag^+ and 1 M NH_3 at pH 11.5. The formation of $Ag(NH_3)_4^{2+}$ was discussed previously.[23] The rate of decay of the $Ag(NH_3)_4^{2+}$ absorption at 270–280 nm was found to depend on the substrate concentration in a manner similar to that presented in Figure 5. The findings are interpreted by reactions 21 and 22. At lower [S] reaction

$$Ag(NH_3)_4^{2+} + S \rightleftarrows [Ag(NH_3)_3S]^{2+} + NH_3 \qquad (21)$$

$$[Ag(NH_3)_3S]^{2+} \rightarrow Ag(NH_3)_2^+ + NH_3 + S^{+}\cdot \qquad (22)$$

21 is the rate-determining step, while at higher [S] reaction 22 becomes rate determining. The values of k_{22} (Table II) are $\sim 4 \times 10^3$ s^{-1} for all four compounds. The rates of complexation k_{21} vary slightly; increased alkyl substitution on the α-carbon causes a more rapid complexation by increasing the density of electrons on the nitrogen available for coordination with the silver.

Three other compounds examined lend further support to this mechanism. Betaine, ethylenediamine, and formic acid did not affect the decay of $Ag(NH_3)_4^{2+}$ and must react with $k \leq 10^4$ M^{-1} s^{-1}. In the case of betaine ($(CH_3)_3N^+CH_2CO_2^-$) complexation through the N is not possible, and oxidation of the carboxyl group in betaine is less favorable than that in glycine. Oxidation of formate ion is thermodynamically favorable, but it does not take place because of the lack of a strong coordinating group. On the other hand, ethylenediamine may replace NH_3 in the $Ag(NH_3)_4^{2+}$, but it lacks the carboxyl group which is the site of oxidation. Therefore, the absence of a detectable reaction with the latter three compounds supports the suggested mechanism for the amino acids. It is apparent that an amino group is necessary as a binding site and a carboxyl group as the site of oxidation.

Summary and Conclusions

The results presented here show that amino acids are oxidized by Ag(II) in a two-step mechanism: first, complexation of the amino acid to the Ag(II), and second, electron transfer from the carboxyl group to the Ag(II) (e.g., reactions 10 and 16). The rates of complexation depend on both the structure of the substrate and the form of the Ag(II) reacting with it. With $Ag(NH_3)_4^{2+}$ at pH 11.5 (Table II) the amino acids coordinate via their basic NH_2 group. The rate of complexation varies somewhat with structure and depends on the electron density on the nitrogen, which is affected by the number of alkyl groups. It is reasonable to assume that the carboxyl group must also coordinate with the Ag(II) before it is oxidized. Once complexation has taken place, the rate of oxidation is very similar for glycine, alanine, aminoisobutyric acid, and aspartic acid. The small variations observed (Table II) can again be rationalized by the electron-donating properties of methyl substituents which facilitate the transfer of an electron from the carboxyl group to the Ag(II).

The kinetic behavior of glycine and aminoisobutyric acid at pH 4.4 shows complexation rate constants $\sim 1.5 \times 10^6$ M^{-1} s^{-1} and oxidation rates $\sim 5 \times 10^3$ s^{-1}. Complexation in this case probably takes place initially through the carboxyl group since the amino group is protonated ($pK_a \approx 10$). Pivalic acid under similar conditions is found to undergo both complexation and oxidation more rapidly. Both of these reactions depend on the density of electrons on the carboxyl group, which is increased by the three methyl groups of pivalic acid as compared with glycine and AIB. Furthermore, pivalic acid does not contain the strong electron-withdrawing NH_3^+ group, and its carboxyl group is mostly protonated at the pH used (4.3). All these differences cause a

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Table II. Rate Constants of Complexation and Oxidation by Ag(II)

Ag(II) species	substrate	pH	k(complexation), M^{-1} s^{-1}	k(oxidation), s^{-1}
$AgOH^+ + Ag^{2+}$	glycine	4.4	$(1.5 \pm 0.3) \times 10^6$	$(5.2 \pm 0.5) \times 10^3$
$AgOH^+ + HOAg^{II}Gly$	glycine	9.0	$(6 \pm 1) \times 10^7$ [a]	$5 \times 10^2 \rightarrow 5 \times 10^1$ [b]
$AgOH^+ + Ag^{2+}$	AIB	4.4	$(1.7 \pm 0.4) \times 10^6$	$(5 \pm 1) \times 10^3$
$AgOH^+ + HOAg^{II}AIB$	AIB	8.8	$(4 \pm 1) \times 10^7$	$(4 \pm 1.5) \times 10^3$
$AgOH^+$	pivalic acid	4.3	$\sim 1 \times 10^8$	$(1 \pm 0.2) \times 10^4$
$AgOH^+ + Ag(OH)_2$	pivalate	8.8	$<10^7$	
$AgOH^+$	succinate	5.6		$(2 \pm 0.5) \times 10^2$
$Ag^{II}NTA$	NTA	10.7		$(2 \pm 0.5) \times 10^3$
$Ag^{II}EDTA$	EDTA	11.0		8 ± 2
$Ag(NH_3)_4^{2+}$	glycine	11.5	$(5 \pm 1) \times 10^5$	$(3 \pm 0.7) \times 10^3$
$Ag(NH_3)_4^{2+}$	alanine	11.5	$(8 \pm 1.5) \times 10^5$	$(5 \pm 1) \times 10^3$
$Ag(NH_3)_4^{2+}$	AIB	11.5	$(2 \pm 0.4) \times 10^6$	$(5 \pm 1) \times 10^3$
$Ag(NH_3)_4^{2+}$	aspartate	11.5	$(1.2 \pm 0.2) \times 10^6$	$(4 \pm 1) \times 10^3$
$Ag(NH_3)_4^{2+}$	betaine	11.5	$\leq 10^4$	
$Ag(NH_3)_4^{2+}$	formate	11.5	$\leq 10^4$	
$Ag(NH_3)_4^{2+}$	ethylenediamine	11.5	$\leq 10^4$ [c]	

[a] This value can be extrapolated to 3×10^8 M^{-1} s^{-1} for the completely basic form of glycine. [b] Value decreases with [Gly], see text. [c] This low value only indicates the lack of oxidation but complexation may have taken place and was not detected.

combined effect of nearly 2 orders of magnitude in the rate of complexation of $(CH_3)_3CCO_2H$ vs. $H_3N^+CH_2CO_2^-$ (or $H_3N^+C(CH_3)_2CO_2^-$).

At pH ~9 the relative reactivities of pivalic acid and the amino acids are reversed. The former reacts much more slowly while the amino acids coordinate rapidly through the basic amino group. A value of 3×10^8 M^{-1} s^{-1} is estimated for the rate constant of complexation with the fully basic form of glycine, which is 2 orders of magnitude higher than that for complexation through the carboxyl group.

The Ag(II) amino acid complexes undergo intramolecular electron transfer, with rates strongly dependent on the structure (Table II). NTA shows a rate of 2×10^3 s^{-1}, while EDTA only 8 s^{-1}. The rate of oxidation of glycine decreases from 500 to 50 s^{-1} upon increasing [Gly]. It appears that these rates depend on the stability of the complex which is expected to affect the redox potential of the Ag(II). EDTA forms a more stable complex than NTA, while the stability of the glycine complex increases with concentration, i.e., with the number of glycine molecules bound to the Ag(II). On the basis of the rates of the EDTA and NTA complexes, the results with glycine may be interpreted as follows. The rate of 50 s^{-1} found at high glycine concentration is for the complex $Ag^{II}(Gly)_2$, which is somewhat similar in structure to the EDTA complex. The higher rates observed at lower [Gly] indicate oxidation through a species containing less glycine, probably $HOAg^{II}Gly$ or $(HO)_2Ag^{II}Gly$. This would further indicate that the more rapid oxidations observed in acid solutions, and also those with $Ag(NH_3)_4^{2+}$, take place via structures containing only one amino acid bound to the Ag(II).

In all the compounds studied the rate of oxidation is found to be relatively low, usually in the range of 10^1 to 10^4 s^{-1}. This rate seems quite slow for an intramolecular electron transfer from the carboxyl group to the Ag(II) bound to it. Such a phenomenon has been noticed previously in the case of oxidation by Cu(III), and several arguments have been advanced to explain it.[27] The main reason may be the lack of overlap between the acceptor and the donor orbitals, as argued previously for the intramolecular electron transfer in various Co(III) benzoato complexes.[31,32]

The possible participation of Ag(III) as an oxidant in the Ag^+–$S_2O_8^{2-}$–RH systems has been excluded[8] on the basis of kinetic data. The present results support this conclusion. Most of the observed complexation and oxidation reactions occurred at time scales shorter than those required for the formation of Ag(III).[23]

In the present study the Ag^+ ion served as a mediator for the one-electron oxidation of the carboxyl group by a hydroxyl radical. Such a reaction does not take place directly to any considerable extent because OH radicals prefer to react by hydrogen abstraction. The silver, therefore, has served as a "catalyst" which binds the two reacting species and makes the electron-transfer route more feasible. Ag^+ can thus be used not only as a catalyst for the initiation of oxidation reactions by certain other oxidants but also for the alteration of the mode of oxidation in certain cases.

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