

Deamination of β -alanine induced by hydroxyl radicals and monovalent copper ions. A pulse radiolysis study

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(Received August 1, 1991; revised October 11, 1991)

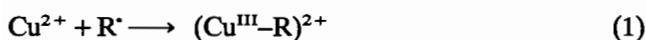
Abstract

Hydroxyl radicals abstract hydrogen atoms from β -alanine (3-aminopropanoate) at the α position to the carboxylate group with specific rate constants of $(4.5 \pm 0.8) \times 10^7$ and $(1.1 \pm 0.2) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ at pH 3 and 6.5, respectively. The carbon-centered free radical (3-amino-2-yl-propanoate) reacts with Cu^+_{aq} to form an organometallic intermediate with a rate constant of $(3.4 \pm 0.7) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. This intermediate decomposes via a first order reaction with a rate constant of $(1.1 \pm 0.2) \times 10^4 \text{ s}^{-1}$ at $\text{pH} > 3.5$ and $(2.7 \pm 0.3) \times 10^4 \text{ s}^{-1}$ at $\text{pH} \leq 3$. A detailed product analysis shows that the yield of carbon dioxide is insignificant and the final stable product is acrylic acid. It is concluded that the complex with the copper-carbon σ -bond decomposes via a β -elimination of ammonia causing degradation of the amino acid. The spectrum of the organometallic intermediate and the factors affecting the mechanism of its decomposition are discussed.

Introduction

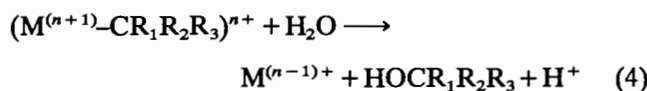
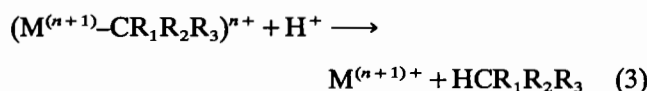
Interest in the reactivity of Cu(I) and Cu(II) complexes towards organic free radicals has increased in recent years due to the role of copper ions in enhancing or in protecting against radiation and free radical damage in biological systems [1]. Some Cu(II) complexes can be oxidized to the corresponding Cu(III) complexes, which are powerful oxidizing species and may cause decarboxylation or deamination of polypeptides and even in some cases dephosphorylation of polynucleotides and DNA [2–4]. Furthermore, many copper complexes may also serve as catalysts in various organic reactions [5].

It has been demonstrated that cupric and cuprous ions and many of their complexes react with many organic free radicals to form transients with a metal-carbon σ -bond [6–15].

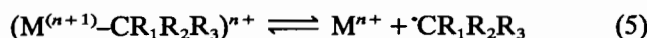


In most cases k_2 is much higher than k_1 , approaching the diffusion controlled limit [7–14]. The decomposition of the transients with the metal-carbon σ -bond has been reported to occur via two main reaction pathways:

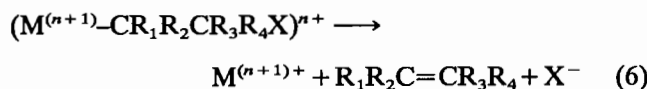
(i) A heterolytic cleavage of the σ -bond:



(ii) A homolytic cleavage of the σ -bond:

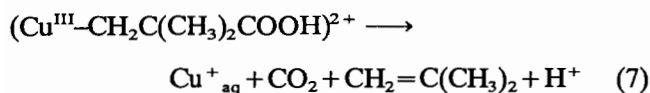


However, when a good leaving group is bound at the β position to the carbon-centered free radical, a third reaction, namely a β -elimination reaction to form an olefin, may take place



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or a decarboxylation process as in the case of $\text{Cu}^{2+}_{\text{aq}}$ and trimethylacetic acid [15]:



Thus, decomposition of complexes with a metal-carbon σ -bond in many cases causes the cleavage of the organic molecule. When these kind of reactions occur in biological systems, they may cause deleterious effects, especially when the decomposition process proceeds via the β -elimination reaction [16].

The reaction of OH^{\cdot} with β -alanine yields two radicals $\cdot\text{CH}(\text{COO}^-)\text{CH}_2(\text{NH}_3^+)$ and $\cdot\text{CH}(\text{NH}_2)\text{CH}_2\text{COO}^-$. These radicals have potentially two good leaving groups, ammonia and carbon dioxide, bound to the carbon atom at the β position to the carbon-centered free radicals. Thus, if copper reacts with these radicals, cleavage of the amino acid may occur via β -elimination processes. This system may serve as a simple and good model for reactions occurring in biological systems, where OH^{\cdot} radicals are generally assumed to be formed via ionizing radiation, the modified Fenton reaction, absorption of UV light and also by many drugs and cytotoxic agents.

Experimental

Materials

All chemicals employed were of analytical grade and were used as received. $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ was prepared according to known procedures [17]. Solutions were prepared with distilled water which was further purified using a Milli-Q water purification system containing three cartridges with a final resistance of $>10 \text{ M}\Omega/\text{cm}$. Cuprous solutions were prepared by dissolving $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ in deaerated solutions containing β -alanine at various pHs in the presence and absence of CuSO_4 . When more than $5 \times 10^{-5} \text{ M}$, $1.0 \times 10^{-4} \text{ M}$ and $1.5 \times 10^{-4} \text{ M}$ cuprous salt were dissolved, the precipitation of the yellow cuprous oxide was observed at pH 7, 5 and 3, respectively. The pH was adjusted by adding HClO_4 or NaOH solutions before adding the cuprous salt.

Irradiation

Pulse radiolysis experiments were carried out with the Varian 7715 linear accelerator at the Hebrew University of Jerusalem. The pulse duration was 0.1–1.5 μs with a 200 mA current of 5 MeV electrons. Irradiations were carried out in a 4 cm spectroil cell using three light passes. A 150 W Xenon arc produced the analyzing light. The detection system included a Bausch & Lomb grating double monochromator model D330/

D331 Mk.II and an IP28 photomultiplier. The signal was transferred through a SONY/TEKTRONIX 390AD programmable digitizer to a micro PDP-11/24 computer which operated the whole system. N_2O -saturated solutions containing 1 mM KSCN were used for dosimetry. The yield of $(\text{SCN})_2^-$ was measured assuming $G((\text{SCN})_2^-) = 6.1$ and $\epsilon_{475} = 7600 \text{ M}^{-1} \text{ cm}^{-1}$. Large doses of 10 Krad have been delivered into small cylindrical glass bulbs (12 ml volume) filled with deaerated solutions and sealed with a rubber septum for gas chromatograph analysis.

Analysis

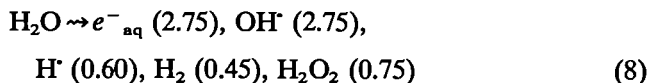
Spectroscopic measurements were carried out using a Hewlett-Packard HP 8452A diode array spectrophotometer. The initial concentration of cuprous ions was determined with the use of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline-disulfonic acid (bathocuproinedisulfonic acid). This compound is very soluble in water, and complete formation of $\text{Cu}(\text{I})$ complex occurs over the pH 3–11. The cuprous complex formed is not oxidized by oxygen, and its molar absorptivity is $12\,250 \text{ M}^{-1} \text{ cm}^{-1}$ at 483 nm [18]. The results show that the initial concentration of the cuprous ions was about 70% of that determined by weight, indicating that the cuprous salt contains cupric ions and also that $\text{Cu}^{+}_{\text{aq}}$ under the experimental conditions disproportionates to Cu^0 and $\text{Cu}^{2+}_{\text{aq}}$.

Carbon dioxide and ammonia as final products were identified by gas chromatography using a Hewlett-Packard model 5890 instrument. The gas samples were taken through the rubber septa with gas-tight syringes and were separated on a $10' \times 1/8''$ stainless steel column packed with poropak Q 80/100 mesh using temperature program starting at 45 $^{\circ}\text{C}$ and heating at a rate of 70 $^{\circ}\text{C}/\text{min}$ to a final temperature of 190 $^{\circ}\text{C}$. The gases were transferred through TCD and FID detectors connected in series. Irradiated N_2O -saturated solutions containing 1 mM $\text{Co}(\text{NH}_3)_6^{3+}$ and 0.1 M formate at pH 4.8 were used for determining the concentrations of CO_2 formed. Under these conditions all the primary radicals produced by the radiation are converted into $\text{CO}_2^{\cdot -}$ radical, which subsequently reduces the metal to form carbon dioxide [19]. The ammonia was identified only qualitatively with the FID detector as its concentration was too low for quantitative analysis with the TCD detector.

The spectrum of the π -complex formed between $\text{Cu}^{+}_{\text{aq}}$ and acrylic acid ($\text{CH}_2=\text{CHCOOH}$) was measured at pH 3 and 5 in deaerated solutions. The Cu^{I} -acrylic acid complex has a spectrum typical for a $d \rightarrow \pi^*$ complex of cuprous ions with olefins [13, 20] with maxima at 252 nm ($\epsilon = 5700 \pm 500 \text{ M}^{-1} \text{ cm}^{-1}$) and 318 nm ($\epsilon = 1400 \pm 200 \text{ M}^{-1} \text{ cm}^{-1}$).

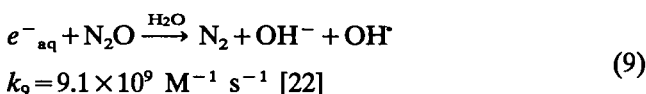
Production of free radicals

The radiolysis of water may be summed up by the following equation:

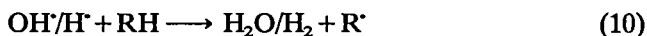


The numbers in parentheses are G values which represent the number of molecules formed per 100 eV energy absorbed in the solution. In concentrated solutions the yields of the primary free radicals are somewhat higher and those of H_2 and H_2O_2 are somewhat lower [21].

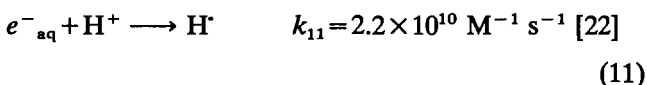
In neutral N_2O -saturated solutions ($[\text{N}_2\text{O}] = 0.022 \text{ M}$) the hydrated electron is converted into the hydroxyl radical via:



The hydroxyl radical and the hydrogen atom react relatively fast with organic solutes (RH) to form organic free radicals via:



In acidic solutions the reaction of e^-_{aq} with H^+ , which produces H^\cdot radicals, becomes important,



but at $\text{pH} > 3$ the contribution of H^\cdot radicals to the total radical yield is less than 10%.

Results

Upon pulse-irradiation of N_2O -saturated solutions containing 0.03–0.1 M β -alanine, the formation of transients absorbing in the range of 300–400 nm was observed (Fig. 1). These intermediates, which were formed within the pulse duration, disappeared via a second order reaction where $2k = (7.9 \pm 1.2) \times 10^8$ and $(1.5 \pm 0.3) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ at pH 3 and 5, respectively. The specific rate constant of the reaction of OH^\cdot with β -alanine was determined using the competition kinetic method [22]. N_2O -saturated solutions containing 0.1 mM KSCN and various concentrations of β -alanine at pH 3 and 6.5 were pulse-irradiated, and the yield of $(\text{SCN})_2^-$ was determined at 475 nm. Using $k(\text{OH}^\cdot + \text{SCN}^-) = 1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ [22], k_{10} for OH^\cdot was determined to be $(4.5 \pm 0.8) \times 10^7$ and $(1.1 \pm 0.2) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ at pH 3 and 6.5, respectively.

When 0.2–1 mM CuSO_4 was added to N_2O -saturated solutions containing 0.03–0.1 M β -alanine, the formation of an unstable intermediate was observed. At pH 5 the spectrum of the species formed was within exper-

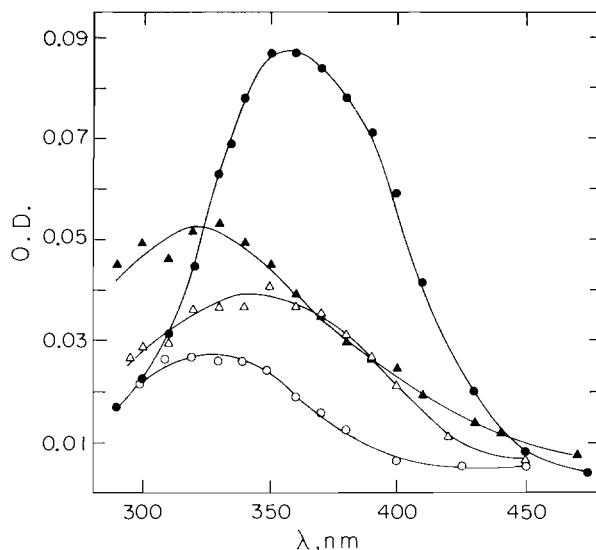


Fig. 1. Absorption spectra obtained at the end of the pulse in irradiated N_2O -saturated solutions containing 0.1 M β -alanine at pH 3 (O); pH 5 (Δ); $5 \times 10^{-4} \text{ M}$ CuSO_4 at pH 3 (\blacktriangle); $1.1 \times 10^{-4} \text{ M}$ Cu^+_{aq} at pH 3, 15 μs after the end of the pulse (\bullet). The optical path length was 12.1 cm and the dose 960 rad/pulse.

imental error identical with that in the absence of cupric ions, whereas at pH 3 the species had a different spectrum (Fig. 1). The kinetics of the formation of the absorbance under these experimental conditions was too fast to be measured. The kinetics of the decomposition of this species was complex being a mix of a first and a second order reaction. However, the half-life of the transient formed was somewhat shorter than that formed in the absence of copper.

Upon dissolving 3.5×10^{-5} to $1.4 \times 10^{-4} \text{ M}$ cuprous salt in N_2O -saturated solutions containing 0.03–0.2M β -alanine at pH 2–7.4, the formation of another intermediate with a different absorption spectrum was observed (Fig. 1). Within experimental error, the spectrum obtained at pH 3 was the same as that obtained at pH 5. The presence of up to 1 mM CuSO_4 had no effect on the spectrum. The kinetics of the formation of the absorbance followed a pseudo first order reaction and the observed rate constant (k_f) was linearly dependent on $[\text{Cu}^+_{\text{aq}}]$ (Fig. 2), independent of $[\beta\text{-alanine}]$ and pH (Table 1). In the presence of cupric ions some increase in k_f was observed at low pHs (Table 1). The decomposition of the transient formed obeyed a first order rate law, with an observed rate constant (k_d) being independent of $[\text{Cu}^+_{\text{aq}}]$, $[\text{Cu}^{2+}_{\text{aq}}]$ and $[\beta\text{-alanine}]$. However, k_d was about 2.5 times higher at $\text{pH} \leq 3$ than that at $\text{pH} > 3.5$ (Table 1). Typical kinetic plots are given in Fig. 3.

N_2O -saturated solutions containing 0.2 M β -alanine with and without $1.4 \times 10^{-4} \text{ M}$ cuprous ions at pH 3 were pulse irradiated with a 10 Krad dose, and the

TABLE 1. Typical yields and rates of formation (k_f) and decomposition (k_d) of transients observed in pulse radiation of N_2O -saturated solutions containing β -alanine and cuprous ions in the absence and presence of cupric ions as measured at 360 nm

[β -ala] (M)	pH	[Cu^{+}_{aq}] (M)	[Cu^{2+}_{aq}] (M)	OD_0	OD_{∞}	k_f (s^{-1})	k_d (s^{-1})
0.1	2.0	5.1×10^{-5}		0.031 ^a	0.022	1.8×10^5	2.7×10^4
0.1	2.5	5.1×10^{-5}		0.054	0.037	1.9×10^5	3.0×10^4
0.1	3.0	7.0×10^{-5}		0.084	0.031	1.9×10^5	2.6×10^4
0.1	3.0	7.0×10^{-5}	5×10^{-4}	0.072	0.021	3.1×10^5	2.8×10^4
0.1	3.0	7.0×10^{-5}	1×10^{-3}	0.070	0.018	4.1×10^5	3.0×10^4
0.1	3.0	3.5×10^{-5}		0.070	0.031	1.3×10^5	1.8×10^4
0.1	3.0	1.1×10^{-4}		0.083	0.030	3.9×10^5	2.8×10^4
0.1	3.0	1.1×10^{-4}	5×10^{-4}	0.080	0.025	5.3×10^5	3.0×10^4
0.03	3.0	1.1×10^{-4}		0.082	0.028	2.0×10^5	2.1×10^4
0.2	3.0	1.1×10^{-4}		0.097	0.037	3.1×10^5	3.3×10^4
0.1	3.0	1.4×10^{-4}	5×10^{-4}	0.080	0.024	4.6×10^5	3.1×10^4
0.1	4.0	7.0×10^{-5}		0.120	0.038	2.1×10^5	1.1×10^4
0.1	5.0	7.0×10^{-5}		0.128	0.044	2.6×10^5	1.0×10^4
0.1	5.0	7.0×10^{-5}	1×10^{-3}	0.092	0.017	2.5×10^5	1.1×10^4
0.1	7.0	4.8×10^{-5}	5×10^{-4}	0.110 ^a	0.032	2.7×10^5	1.8×10^4
0.1	7.4	3.5×10^{-5}		0.095 ^a	0.028	9.0×10^4	1.0×10^4

^aMeasured at 375 nm.

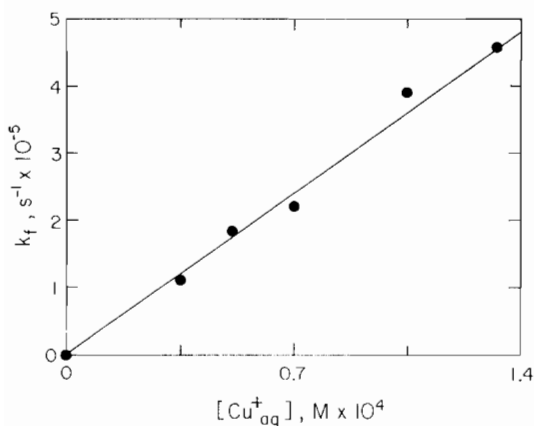


Fig. 2. The observed rate constant of the formation of the absorbance (k_f) as a function of [Cu^{+}_{aq}] in N_2O -saturated solutions containing 0.1 M β -alanine at pH 2-7.

gases formed were analyzed using gas chromatography. The yield of carbon dioxide in the absence of cuprous ions was $G(CO_2) \leq 1.1$, and in their presence $G(CO_2) \leq 0.6$. As shown in Fig. 3, the absorption does not decay to zero. The absorption spectrum of the final products differed from that of the transient formed. We have measured the spectrum after it has been irradiated by several pulses and found that it was identical to that of the π -complex formed between Cu^{+}_{aq} and acrylic acid in the wavelength region studied.

Discussion

It has been shown, using the ESR technique, that in slightly acidic solutions OH^{\cdot} abstracts a hydrogen

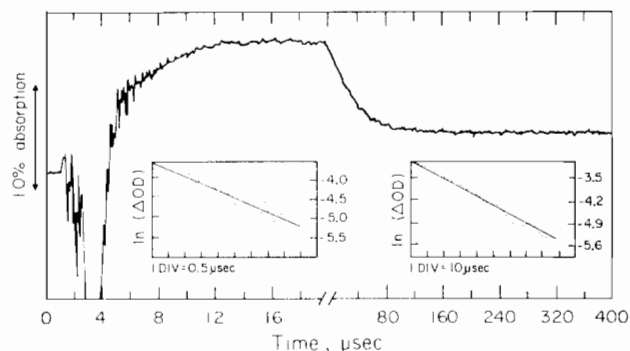
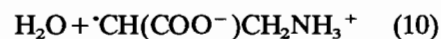
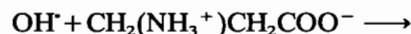
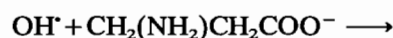


Fig. 3. Typical kinetic plots of the formation and decay of the signal formed in N_2O -saturated solutions containing 0.1 M β -alanine and 1.5×10^{-4} M Cu^{+}_{aq} at pH 3 at 380 nm. The optical path length was 12.1 cm, and the dose 960 rad/pulse. The inset contains fits of the formation and the decomposition reactions to a first order rate law.

atom only at the carbon atom α to the carboxylate group [23].



Only at relatively high pHs (above the pK_a of the amine group) was the formation of the radical at the carbon atom β to the carboxylate group reported.

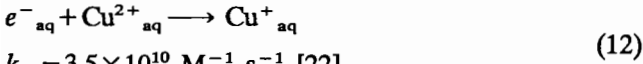


Thus, irradiation of solutions containing β -alanine at $pH < 8$ yields only the carbon-centered free radical at the α position to the carboxylate group with

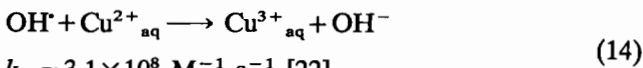
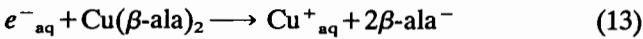
$k_{10} = (4.5 \pm 0.8) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and $(1.1 \pm 0.2) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ at pH 3 and 6.5, respectively.

In N_2O -saturated solutions containing 0.03–0.2 M β -alanine and 3.5×10^{-5} to 1.4×10^{-4} M Cu^+_{aq} and/or 0.5–1 mM $\text{Cu}^{2+}_{\text{aq}}$, only the cupric ions are complexed by β -alanine. The relative concentration of the various species formed depends on pH and [β -alanine]. Using the equilibria constants given in ref. 24, we calculated the contribution of the various species under our experimental conditions (Table 2).

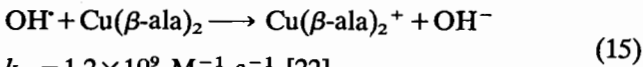
$\text{Cu}^{2+}_{\text{aq}}$, $\text{Cu}(\beta\text{-ala})_2$ and Cu^+_{aq} may compete with N_2O and β -alanine for e^-_{aq} , OH^- and H^{\cdot} radicals via the following reactions:



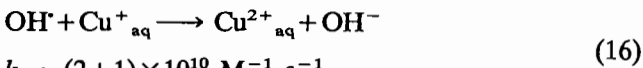
$$k_{12} = 3.5 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \quad [22]$$



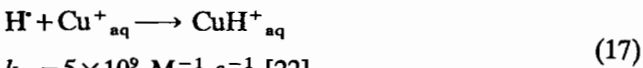
$$k_{14} = 3.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1} \quad [22]$$



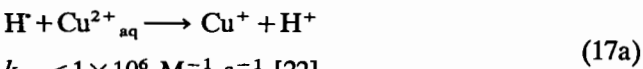
$$k_{15} = 1.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \quad [22]$$



$$k_{16} = (2 \pm 1) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$$



$$k_{17} = 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \quad [22]$$



$$k_{17a} \leq 1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1} \quad [22]$$

The specific rate constant of reaction (13) has not yet been determined, but it is probably similar to that of other complexes of copper(II) with amino acids ($6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ at neutral pH) [22]. Thus, under the condition where $[\text{Cu}^{2+}_{\text{aq}}] \leq 1 \text{ mM}$, the majority of the hydrated electrons react with N_2O to yield OH^- via reaction (9). $k_{16} = (2 \pm 1) \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ has been determined in N_2O -saturated solutions containing about 0.2 mM CuCl and 2 M NaCl at pH 5.8 [22, 25]. This value seems to be too high for our system because increasing the

concentration of β -alanine from 0.03 to 0.2 M only slightly affected the yield of the transient formed (see below). The contribution of H^{\cdot} radicals to the total radical yield is less than 10% at $\text{pH} \leq 3$. Thus as for H^{\cdot} $k_{10} = 3.4 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ [22], only in the presence of cuprous ions will H^{\cdot} disappear via reaction (17) to yield $\text{Cu}^{2+}_{\text{aq}}$. Only at low pHs (< 3) do reactions (11) and (17) become important. Therefore under most of our experimental conditions all the primary radicals formed by the radiation are converted into the aliphatic radical via reaction (10). In the presence of cuprous ions at $\text{pH} \geq 3$ only about 90% of all the primary radicals are converted into the aliphatic radicals due to reaction (17). However, the decrease in the initial $[\text{Cu}^+_{\text{aq}}]$ due to reaction (17) was insignificant under the experimental conditions where the yield of all the primary radicals $\leq 6 \mu\text{m}$.

When N_2O -saturated solutions containing β -alanine and CuSO_4 were pulse-irradiated, only at low pHs was a transient with a different spectrum than that of the aliphatic radical formed (Fig. 1). As at low pHs β -alanine does not bind $\text{Cu}^{2+}_{\text{aq}}$ (Table 2), it is suggested that $\text{Cu}^{2+}_{\text{aq}}$ reacts with the aliphatic radical to form $(\text{Cu}^{\text{III}}\text{-R})^{2+}$, whereas at high pHs the rate of the reaction of the $\text{Cu}(\text{II})$ complex with the radical is too low to compete with the dimerization of the radical. We were unable to measure the rate of formation of $(\text{Cu}^{\text{III}}\text{-R})^{2+}$ because the difference in the absorbance between $(\text{Cu}^{\text{III}}\text{-R})^{2+}$ and the aliphatic radical was too small (Fig. 1).

The results in the presence of Cu^+_{aq} suggest that at $\text{pH} < 8$ Cu^+_{aq} reacts with 3-amino-2-yl-propanoate to form a complex with a copper-carbon σ -bond.



The absorption spectrum of this organometallic complex has a maximum at $360 \pm 5 \text{ nm}$ ($\epsilon_{\text{mas}} = (1500 \pm 250) \text{ M}^{-1} \text{ cm}^{-1}$), which is a typical spectrum for a complex with a Cu^{II} -carbon σ -bond [8, 11, 13]. It is possible that though the free radical has a pK_a in the pH range studied, as indicated by the different rate of the dimerization at different pHs, the transients with the

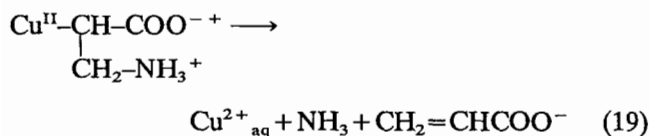
TABLE 2. The relative concentration of the $\text{Cu}(\text{II})$ species present in aqueous solutions containing β -alanine (L^-) at various pHs

[β -alanine] (M)	pH	$\text{Cu}^{2+}_{\text{aq}}$	CuL^+	CuL_2	CuLH^{2+}	$\text{Cu}(\text{LH})L^+$	$\text{Cu}(\text{LH})_2^{2+}$
0.10	3	0.95			0.05		
0.03	3	0.88			0.11		
0.10	3	0.65	0.016		0.26		0.08
0.20	3	0.43	0.021		0.34		0.21
0.10	5	0.05	0.520	0.21	0.08	0.03	0.10
0.10	7		0.024	0.97			

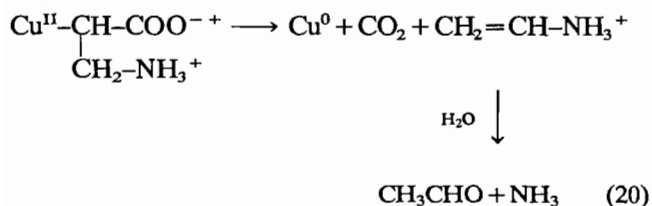
Cu^{II} -carbon σ -bond exist only in the basic form due to the inductive effect of the copper ion. The specific rate constant of reaction (18) was determined from the slope of the line in Fig. 2 to be $(3.4 \pm 0.7) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. This value is similar to other reported values for the reaction of Cu^+_{aq} with various organic free radicals yielding $(\text{Cu}^{\text{II}}-\text{R})^+$ [7–14]. The observed rate constant of the transient formation, k_t , increased with increasing $[\text{Cu}^{2+}_{\text{aq}}]$ at low pHs (Table 1). We assume that the increase in k_t at low pH is due to the formation of $(\text{Cu}^{\text{III}}-\text{R})^{2+}$, which was not observed at high pH. From the difference in k_t obtained in the presence and in the absence of CuSO_4 , a value of $2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ was estimated for the rate constant of the reaction of $\text{Cu}^{2+}_{\text{aq}}$ with 3-amino-2-yl-propanoate. This value is similar to other reported values for the reaction of $\text{Cu}^{2+}_{\text{aq}}$ with various aliphatic free radicals [7–14].

The kinetics of the decomposition of $(\text{Cu}^{\text{II}}-\text{R})^+$ obeyed a first order rate law. Two possible reaction mechanisms can account for the decomposition process:

(i) A deamination process:



(ii) A decarboxylation process:



In order to distinguish between these two processes, a detailed product analysis had been carried out. As the measured yield of carbon dioxide was insignificant, ammonia was identified qualitatively and the absorption spectrum of the irradiated solutions was found to be the same as that of the π -complex of $\text{Cu}(\text{I})$ -acrylic acid, it is concluded that mainly reaction (19) occurs where $k_{19} = (1.1 \pm 0.2) \times 10^4$ and $(2.7 \pm 0.3) \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at $\text{pH} > 3.5$ and ≤ 3 , respectively.

The value of k_{16} in our system must be by at least an order of magnitude lower than that reported for the reaction of OH^\cdot radicals with CuCl in the presence of 2 M NaCl at $\text{pH} 5.8$ [25]. If this value was valid for our cuprous salt, then Cu^+_{aq} would have competed efficiently with β -alanine for OH^\cdot radicals, and the yield of $(\text{Cu}^{\text{II}}-\text{R})^+$ would have been strongly dependent on β -alanine concentration. For example, at $\text{pH} 3$ the yield of the transient formed should have decreased by 60% at 0.03 M β -alanine as compared to that obtained at 0.2 M β -alanine. As this is not the case (Table 1) and the yield of the transient

formed decreased only by about 20%, we estimated $k_{16} = 3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for our cuprous salt.

Conclusions

In the present study we have demonstrated that when 3-amino-2-yl-propanoate is formed in the presence of cuprous ions, a fast deamination process takes place. In this case a transient with a Cu^{II} -carbon σ -bond is formed followed by a β -elimination of ammonia causing the degradation of the amino acid. In the absence of cuprous ions the radical most probably decays via a dimerization reaction.

It is of interest to note that the rate of the β -hydroxyl elimination from $(\text{L}_m\text{Cu}^{\text{II}}-\text{CR}_1\text{R}_2\text{CR}_3\text{R}_4\text{OH})^+$ is acid catalyzed and obeys eqn. (21) [11, 12].

$$k_{\text{obs}} = k_0 + k_{\text{H}}[\text{H}_3\text{O}^+] \quad (21)$$

We did not expect that the β -elimination of ammonia would be acid catalyzed as under all the experimental conditions the ammonia was protonated. However, though the bond energy of C–O is considerably larger than that of C–N [26], k_{19} is relatively low as compared to $k_{\text{H}} > 1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, which is the case for Cu^+_{aq} and various aliphatic radicals [11, 12]. We have no explanation for this result though it is tempting to speculate that the non-bonding electrons on the eliminated water molecule are somehow involved in the reaction mechanism.

Acknowledgements

This work was supported by The Israel Academy of Sciences, The GSF Forschungszentrum für Umwelt und Gesundheit, GmbH, Neuherberg, The Council for Higher Education and The Israel Atomic Energy Commission.

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