# **Copper-Catalyzed Radiolytic Reduction of CO<sub>2</sub> to CO in Aqueous Solutions**

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Radiolysis of aqueous solutions containing CO2 and Cu(II) ions under reducing conditions leads first to reduction of the Cu(II) and then to formation of CO. Experiments under various conditions show that although Cu(II) was often reduced to colloidal Cu(0) particles, formation of CO requires the presence of Cu(I). It also requires that  $CO_2$  be first reduced to the  $CO_2^-$  radical. The  $CO_2^-$  radical was produced radiolytically by reaction of  $CO_2$  with  $e_{aa}$  or by reaction of formate ions with H<sup>•</sup> and •OH radicals and photochemically by reaction of formate with the acetone triplet. The 'CO<sub>2</sub><sup>-</sup> radicals are reduced to CO via addition to Cu(I) and subsequent reaction of the product with another Cu(I). The first reaction produces CuCO<sub>2</sub>, which undergoes protonation at pH < 4. The reaction of the neutral CuCO<sub>2</sub> with Cu(I) leads to reduction of the copper to form Cu<sub>2</sub><sup>+</sup> and subsequently Cu(0) particles. However, the reaction of the protonated form,  $CuCO_2H^+$ , with Cu(I) leads to oxidation of the copper and formation of CO in the form of the CuCO<sup>+</sup> complex. After most of the copper is converted into CuCO<sup>+</sup>, subsequent reactions involve this species instead of Cu<sup>+</sup> and lead to further production of CO. From pulse radiolysis measurements, the rate constants for the reactions of the  ${}^{\circ}CO_{2}^{-}$  radicals with Cu<sup>+</sup> and CuCO<sup>+</sup> were found to be  $\approx 1 \times 10^9$  and  $(1.5 \pm 0.4) \times 10^8$  L mol<sup>-1</sup> s<sup>-1</sup>, respectively. The protonated adduct formed by the latter reaction at pH 3.4, Cu(CO)CO<sub>2</sub>H<sup>+</sup>, reacts with CuCO<sup>+</sup> with a rate constant  $\approx 5$  $\times$  10<sup>5</sup> L mol<sup>-1</sup> s<sup>-1</sup> to produce more CO. It also undergoes first-order decomposition and second-order decay reactions.

#### Introduction

Photochemical reduction of  $CO_2$  has been explored as a means of energy storage.<sup>1</sup> The process was catalyzed in either homogeneous or heterogeneous systems and the  $CO_2$  was reduced in most cases to CO and/or formic acid.<sup>2,3</sup> A few experiments demonstrated photoreduction of  $CO_2$  to methane on the surface of metal colloids.<sup>4</sup> Electrochemical reduction of  $CO_2$  led to production of formate on various metallic electrodes, while CO was formed on Ag and Au, and hydrocarbons were formed on Cu electrodes.<sup>5,6</sup> More recently, additional reduction products were identified following electrolysis on Cu, including  $C_2$  and  $C_3$  alcohols and aldehydes.<sup>7</sup> Along with the electrochemical reduction of  $CO_2$ , copious amounts of H<sub>2</sub> were also produced. In recent studies, using alkaline methanol as the electrolyte, the production of H<sub>2</sub> was suppressed while CO<sub>2</sub> was efficiently reduced to CO, formate, methane, and ethylene.<sup>8</sup>

The present study was undertaken to examine whether  $CO_2$  can be reduced on the surface of colloidal copper particles in aqueous solutions and whether reduction can be carried out beyond the CO stage. Photochemical and radiolytic reduction methods were used. In the first experiments, colloidal copper particles were prepared by radiolytic reduction of CuSO<sub>4</sub> in deoxygenated aqueous solutions containing 2-propanol, to create reducing conditions, and poly(vinyl alcohol), to stabilize the metal colloid, similar to the conditions used in earlier studies.<sup>9–11</sup> In subsequent experiments, the conditions were varied to include  $CO_2$  and to study its reduction mechanism.

#### **Experimental Section**<sup>12</sup>

Most of the compounds used were analytical grade reagents from Baker or Mallinckrodt. Poly(vinyl alcohol) (PVA, M.W. 14 000, 100% hydrolyzed) was from Aldrich. Water was purified with a Millipore Super-Q system. The solutions were saturated with Ar (ultrahigh purity), CO<sub>2</sub> (Matheson, 99.99%) (~36 mmol  $L^{-1}$ ), or CO (Air Products, C.P. Grade) (~1.1 mmol  $L^{-1}$ ). Gamma radiolysis was carried out in one of two Gammacell 220 60Co sources with dose rates of 2.1 and 7.0 kGy/h. Photolysis was performed with an ILC Technology 300 W xenon lamp, using a water filter to absorb the IR. Absorption spectra before and after irradiation were recorded with a Cary 3 spectrophotometer. The gases (CO<sub>2</sub>, CO, H<sub>2</sub>, CH<sub>4</sub>) were analyzed by gas chromatography (Carboxen-1000 column, thermal conductivity detector) by sampling the headspace. The total yields were calculated from the known volumes of the solution and the headspace and the known solubilities.<sup>13</sup> Formate ions were analyzed by a Dionex DX-500 ion chromatograph using an AS-11 column and NaOH solutions as eluent. Pulse radiolysis experiments were carried out with 1  $\mu$ s pulses of 6 MeV electrons from a Varian linear accelerator; other details were as described before.14 All experiments were performed at room temperature,  $(21 \pm 2)$  °C. The values of the yields, molar absorption coefficients, and rate constants are reported with their estimated overall standard uncertainties.

### **Results and Discussion**

Preliminary experiments with CO<sub>2</sub>-saturated aqueous solutions containing CuSO<sub>4</sub>, 2-PrOH, and PVA showed production of a reddish copper colloid and then production of CO. To

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understand the relation between these two observations, we examined the spectral evolution during the formation of copper colloids under various conditions and their dependence on the presence of  $CO_2$ .

Colloidal particles of metallic copper were prepared by radiolytic reduction of CuSO<sub>4</sub> in Ar-saturated aqueous solutions containing 2-PrOH, to convert the H<sup>•</sup> and <sup>•</sup>OH radicals into reducing species, and PVA to stabilize the colloid (using [PVA monomer]/[Cu ions] = 20). This procedure is similar to that used in previous studies.<sup>9–11</sup> The copper colloid exhibits a broad absorption between 200 and 800 nm with the characteristic plasmon absorption peak at 590 nm (Figure 1a). The absorption increases with irradiation dose, after an initial delay, and levels off at doses above 3 kGy (Figure 1b). A similar experiment with a CO<sub>2</sub>-saturated solution, however, led to the development of a different spectrum (Figure 1c), with a weaker peak at 590 nm and nearly flat absorption between 300 and 800 nm, but with a higher peak at 275 nm developing with a different time profile (Figure 1d). The final absorption in Figure 1a remained practically unchanged after prolonged irradiation but that in Figure 1c decreased and the copper precipitated. However, upon exposure to air, all the final spectra reverted to the original spectra.

Radiolytic production of copper colloids in CuSO<sub>4</sub>/2-PrOH/ PVA solutions could be carried out in acidic solutions (2.5 <pH < 6) but at higher pH the intermediate Cu(I) precipitated. To overcome this difficulty we used ammonia solutions. Figures 2a and 2b show the production of the copper colloid in 0.1 mol  $L^{-1}$  NH<sub>4</sub>OH solution at pH 11. The starting material is in the form of Cu(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup>, which has a UV absorption. Radiolytic reduction led first to reduction of all the Cu(II) to Cu(I), as monitored by the decrease in absorbance at 263 nm (G = 5.8 $\times$  10<sup>-7</sup> mol J<sup>-1</sup>), and only then was the Cu(I) reduced to form the metallic particles, with an absorption peak at 561 nm. This spectrum (Figure 2a) remained unchanged upon prolonged irradiation (with a dose >10 times greater than the dose required to produce the colloid). Exposure to air, however, led to oxidation of the colloidal copper in two stages, first to Cu(I) and more slowly to Cu(II). When the Cu(NH<sub>3</sub>)<sub>4</sub><sup>2+/2</sup>-PrOH/PVA solution was bubbled with CO<sub>2</sub> until its pH decreased to 7, the peak of the Cu(II) shifted to 276 nm and it decreased upon radiolysis with a similar yield ( $G = 5.7 \times 10^{-7} \text{ mol J}^{-1}$ ) (Figure 2c,d). Further irradiation led to production of colloidal Cu particles but the spectrum was quite different from that observed under Ar.

Prolonged irradiation of the CO<sub>2</sub>-saturated solutions (at pH 3.8 without ammonia and at pH 7 with ammonia) led to production of CO. This process began after the solution was irradiated with the dose required to reduce all the Cu(II), it continued with a slope corresponding to a radiolytic yield  $G \approx$  $2 \times 10^{-7}$  mol J<sup>-1</sup>, but after a large dose it stopped (Figure 3). In the same solution at pH 3.8, H<sub>2</sub> production began with no delay and continued linearly with dose,  $G \approx 1.3 \times 10^{-7}$  mol  $J^{-1}$  (Figure 3). This radiolytic yield of  $H_2$  is the sum of the primary yield from the radiolysis of water ( $G_{\rm H_2} = 0.45 \times 10^{-7}$ mol J<sup>-1</sup>), the yield of H<sup>•</sup> atoms, which react with 2-PrOH to form H<sub>2</sub>, ( $G_{\rm H} = 0.6 \times 10^{-7} \text{ mol J}^{-1}$ ), about 6% of the  $e_{\rm aq}^-$  that react with H<sup>+</sup> to form H• atoms ( $G_{\rm H} \approx 0.17 \times 10^{-7} \text{ mol J}^{-1}$ ), and possibly small amounts from the radiolysis of the 2-PrOH component. Small amounts of CH<sub>4</sub> were also detected (G  $\approx$  $0.08 \times 10^{-7}$  mol J<sup>-1</sup>) but the yield was not increased in the presence of Cu and is assumed to be due totally to the radiolysis of 2-PrOH.15 In addition to these gaseous products, small amounts of formic acid were detected in the solution, with a



**Figure 1.** Growth of optical absorption upon  $\gamma$ -irradiation of aqueous solutions containing CuSO<sub>4</sub> (0.5 mmol L<sup>-1</sup>), PVA (10 mmol L<sup>-1</sup>, molarity in terms of monomer units), and 2-PrOH (0.7 mol L<sup>-1</sup>); (a) Ar-saturated, pH 5, spectra with increasing absorbance in the visible range were recorded after irradiation with the following doses: 0, 450, 600, 900, 1360, 1820, and 4550 Gy; (b) dose dependence of the 590 nm absorbance for the experiment in a; (c) CO<sub>2</sub>-saturated, pH 3.8, spectra with increasing absorbance at 270 nm were recorded after irradiation with the following doses: 0, 300, 600, 900, 1360, 1820, and 4550 Gy; (d) dose dependence of the 590 nm were recorded after irradiation with the following doses: 0, 300, 600, 900, 1360, 1820, and 4550 Gy; (d) dose dependence of the absorbance at 275 nm ( $\bigcirc$ ) and 590 nm ( $\bullet$ ) for the experiment in (c).

radiolytic yield  $G \approx 0.1 \times 10^{-7}$  mol J<sup>-1</sup>, i.e., < 10% of the yield of CO. However, in the absence of copper, the yield of formic acid was  $G = 0.5 \times 10^{-7}$  mol J<sup>-1</sup> but the yield of CO was negligible ( $\approx 0.01 \times 10^{-7}$  mol J<sup>-1</sup>). These results indicate



**Figure 2.** Changes in optical absorption upon  $\gamma$ -irradiation of aqueous solutions containing CuSO<sub>4</sub> (0.5 mmol L<sup>-1</sup>), PVA (10 mmol L<sup>-1</sup>), NH<sub>4</sub>-OH (0.1 mol L<sup>-1</sup>), and 2-PrOH (0.7 mol L<sup>-1</sup>); (a) Ar-saturated, pH 11, spectra recorded after irradiation with the following doses: 1, 0; 2, 520; 3, 870; 4, 1340; 5, 1800; 6, 2270; 7, 3140 Gy; (b) dose dependence of the absorbance at 263 (O) and 561 ( $\bullet$ ) nm for the experiment in (a); (c) CO<sub>2</sub>-saturated, pH 7, spectra recorded after irradiation with the following doses: 1, 0; 2, 290; 3, 580; 4, 1160; 5, 1590; 6, 2310; 7, 4370; 8, 6100; 9, 16 300 Gy; (d) dose dependence of the absorbance at 276 nm (O) and 578 nm ( $\bullet$ ) for the experiment in (c).

that Cu affects the yields of CO and formic acid but is not involved in the production of  $H_2$  and  $CH_4$ . Formic acid is produced by disproportionation of  ${}^{\circ}CO_2{}^{-}$  radicals in acidic aqueous solutions, where no CO is formed. In the presence of



**Figure 3.** Radiolytic production of CO ( $\bullet$ ) and H<sub>2</sub> (O) in CO<sub>2</sub>-saturated aqueous solution containing CuSO<sub>4</sub> (0.5 mmol L<sup>-1</sup>), PVA (10 mmol L<sup>-1</sup>), and 2-PrOH (0.7 mol L<sup>-1</sup>). The yields are given in mmol L<sup>-1</sup> and represent the total amount of the gas as if it remained completely in the aqueous phase.

Cu, production of formic acid is strongly diminished and CO is formed instead.

Addition of 0.1 mol L<sup>-1</sup> acetone to the CuSO<sub>4</sub>/2-PrOH/PVA/ CO<sub>2</sub> solution suppressed the production of CO completely. Since acetone reacts rapidly with the hydrated electron and thus prevents its reaction with CO<sub>2</sub>, this result indicates that production of  $^{\circ}CO_2^{-}$  radicals is necessary for the formation of CO. Further evidence for this conclusion was obtained from photochemical experiments. A mixture of acetone and 2-PrOH is known<sup>16</sup> to produce the (CH<sub>3</sub>)<sub>2</sub>COH radical upon UV photolysis. Photolysis of deoxygenated CuSO<sub>4</sub> solutions containing 0.7 mol  $L^{-1}$  acetone, 0.7 mol  $L^{-1}$  2-PrOH, and 10 mmol  $L^{-1}$  PVA led to the production of colloidal copper. The spectra monitored under Ar and under CO<sub>2</sub> were identical and no CO was detected. This indicates that formation of  $^{\circ}CO_{2}^{-}$  radicals is necessary for the production of CO. To produce •CO<sub>2</sub><sup>-</sup> radicals by photolysis we added formic acid. The acetone triplet abstracts hydrogen from formic acid to form  $^{\circ}CO_2^{-}$ . Under these conditions, CO was detected as a product of photolysis and the absorption spectrum of the copper was similar to that observed in  $\gamma$ -irradiated CO<sub>2</sub>-saturated solutions.

The above results lead to the conclusion that  $^{\circ}CO_2^{-}$  radicals are a necessary intermediate for the production of CO but do not shed light on the copper species involved in this process. It is clear from Figures 1 and 2 that the spectra of the copper species observed under CO<sub>2</sub> are different from those observed under Ar. To ascertain that the spectral differences are not due solely to the change in pH and to characterize the various absorbing species we carried out additional experiments in the presence and absence of PVA.

A clear difference between the spectra in the presence and absence of  $CO_2$  (in both Figures 1 and 2) is the flat absorbance extending to 800 nm that is observed only under  $CO_2$ . Such a flat absorbance is typically due to light scattering by fine particles. Since this is observed only in the presence of  $CO_2$  it is probably due to insoluble Cu(I) carbonate. In fact, its level was more pronounced at increased bicarbonate concentration or increased pH and in all  $CO_2$ -saturated solutions a precipitate appeared after prolonged irradiations.

Another spectral feature that is observed only under CO<sub>2</sub> is the relatively sharp peak at 275 nm. This peak was found to be due to a Cu(I)CO complex. This assignment was confirmed by an experiment with CO-saturated solutions containing 0.5 mmol  $L^{-1}$  CuSO<sub>4</sub>, 10 mmol  $L^{-1}$  PVA, and 0.7 mol  $L^{-1}$  2-PrOH. Irradiation of such solutions led to production of the 275-nm absorption but no absorption at all from 330 to 800 nm.<sup>17</sup> The absorbance at 275 nm reached its maximum after a dose of 1000 Gy, when all the Cu(II) was reduced to Cu(I). From the absorbance at this level we calculate a molar absorption coefficient for the CuCO<sup>+</sup> species  $\epsilon_{275} = 2.4 \times 10^3$  L mol<sup>-1</sup> cm<sup>-1</sup>. By using this  $\epsilon$  value, and from the absorbance buildup vs dose, we calculate the radiolytic yield for formation of this product  $G = 6.0 \times 10^{-7}$  mol J<sup>-1</sup>. This value is in line with the expected reduction of Cu(II) by all  $e_{aq}^{-}$  and (CH<sub>3</sub>)<sub>2</sub>COH radicals and indicates that the Cu(I) produced is efficiently coordinated to CO. Production of the species absorbing at 275 nm was also evident when the CO-saturated solution was reduced with zinc amalgam instead of radiolysis.

The CuCO<sup>+</sup> complex was produced at much lower yields in irradiated ammonia solutions because the large excess of ammonia shifts the equilibrium toward  $[Cu(NH_3)_2]^+$ . Aside from that case, CuCO<sup>+</sup> was formed in all irradiated solutions in which CO was formed, i.e., solutions containing either CO<sub>2</sub> or formate, independent of the presence of PVA. In all these solutions where CuCO<sup>+</sup> was formed, its radiolytic yield was  $G \approx 2 \times 10^{-7}$  mol J<sup>-1</sup>.

Previous results<sup>10</sup> with Ar-saturated formate solutions at pH 7.3 did not indicate formation of CuCO<sup>+</sup>. To find the cause for this apparent discrepancy, we examined the effect of formate concentration and pH. We found that production of CuCO<sup>+</sup> was pronounced whether the concentration of formate was 5 mmol  $L^{-1}$ , as in ref 10, or 0.1 mol  $L^{-1}$ , as in the present study. However, it was pronounced only at pH  $\leq$  4 while at pH  $\geq$  5 radiolysis led predominantly to production of colloidal copper with only intermediate formation of CuCO<sup>+</sup>. Production of colloidal copper was also evident in the absence of PVA, although its long-term stability may be limited and was not examined in these experiments.

Radiolysis experiments with CO2-saturated solutions containing CuSO<sub>4</sub> and 0.1 mol  $L^{-1}$  HCO<sub>2</sub>H/HCO<sub>2</sub><sup>-</sup> at pH 3.4 in the absence of PVA show the development of the optical absorption at 275 nm (Figure 4a) and the production of CO and H<sub>2</sub> (Figure 4b) as a function of dose. Unlike the results in Figures 1c and 3, radiolytic production of CO in this experiment continued linearly with dose up to very high doses and no copper colloid (i.e., no absorbance at 300 to 800 nm) was formed. In the early stages of radiolysis Cu(II) was reduced to Cu(I), then CuCO<sup>+</sup> was formed, and then CO was produced in excess of copper and was released into the solution and gas phases. Production of CO began after the Cu(II) was converted into CuCO<sup>+</sup> and continued linearly with dose, with a yield  $G(CO) = 3.3 \times 10^{-7}$ mol J<sup>-1</sup> (Figure 4b).  $G_{\text{H}_2}$  was  $\approx 1 \times 10^{-7}$  mol J<sup>-1</sup> (Figure 4b). After a considerable amount of CO was produced, we analyzed the remaining amounts of formate and CO<sub>2</sub> and found that both of these compounds were consumed approximately to the same extent. This is in line with the expected reactions of formate with H<sup>•</sup> and •OH radicals ( $G = 3.4 \times 10^{-7} \text{ mol J}^{-1}$ ) and of  $CO_2$  with  $e_{aq}^-$  ( $G = 2.8 \times 10^{-7} \text{ mol J}^{-1}$ ), all reactions leading to formation of  ${}^{\bullet}CO_2^{-}$ . Moreover, in these experiments, the pH of the solution increased, in line with the overall consumption of two protons upon reduction of CO<sub>2</sub> to CO. In contrast, when 2-PrOH was used instead of formate, and metallic copper was produced along with CO, the pH decreased, in line with the release of two protons upon reduction of  $Cu^{2+}$  to  $Cu^{0}$ .

On the basis of all the above results and the mechanism proposed<sup>10</sup> for the production of colloidal copper from Cu<sup>2+</sup> ions we can outline the mechanism of CO formation in the present systems. The H<sup>•</sup> atoms and <sup>•</sup>OH radicals produced by



**Figure 4.** Radiolysis of CO<sub>2</sub>-saturated aqueous solutions containing CuSO<sub>4</sub> (0.25 mmol L<sup>-1</sup>) and HCO<sub>2</sub>H/HCO<sub>2</sub><sup>-</sup> (0.1 mol L<sup>-1</sup>) at pH 3.4; (a) spectra with increasing absorbance at 275 nm were recorded after irradiation with the following doses: 0, 210, 250, 830, 1250, 1660, and 16,650 Gy; the insert shows the growth of absorbance at 275 nm with dose; (b) yield of H<sub>2</sub> ( $\bigcirc$ ) and CO ( $\bigcirc$ ) as a function of dose.

water radiolysis react with 2-PrOH or formate, while  $e_{aq}^{-}$  reacts mostly (>90%) with CO<sub>2</sub> and partially with copper ions. Cu<sup>2+</sup> ions are reduced by  $e_{aq}^{-}$ , by the (CH<sub>3</sub>)<sub>2</sub>COH radicals derived from 2-PrOH, and by the °CO<sub>2</sub><sup>-</sup> radicals formed from formate and CO<sub>2</sub>, to produce Cu<sup>+</sup> ions. These ions are unstable in the absence of suitable ligands. They are much more reactive than Cu<sup>2+</sup> toward (CH<sub>3</sub>)<sub>2</sub>COH and °CO<sub>2</sub><sup>-</sup> radicals and react to form adducts.<sup>10</sup> Direct reduction of Cu<sup>+</sup> to Cu<sup>0</sup> by these radicals is not possible, because of the very negative potential of the latter species. Therefore, it has been suggested<sup>10</sup> that metallic copper is formed via a reaction of the organo-copper species with an additional Cu<sup>+</sup>. For example,

$$Cu^{+} + {}^{\bullet}CO_{2}^{-} \rightarrow CuCO_{2}$$
(1)

$$CuCO_2 + Cu^+ \rightarrow Cu_2^+ + CO_2$$
 (2)

The Cu<sub>2</sub><sup>+</sup> grows into metallic particles by subsequent disproportionation and reduction reactions.<sup>10</sup> The reaction of  $^{\circ}CO_2^{-}$  radicals with Cu(I) was reported to be extremely rapid to form CuCO<sub>2</sub>, which absorbs at 480 nm at pH 7.<sup>10</sup> At pH 4 the peak of the adduct absorption was shifted to 385 nm and the adduct was presumably protonated, CuCO<sub>2</sub>H<sup>+</sup>. From the pH dependence of colloidal copper production we conclude that reaction 2 takes place when the adduct is in its neutral form, but when the adduct is protonated Cu<sup>+</sup> is oxidized rather than reduced, leading to direct formation of the stable CuCO<sup>+</sup>.

$$CuCO_2H^+ + Cu^+ \rightarrow CuCO^+ + OH^- + Cu^{2+} \qquad (3)$$

This mechanism is also in line with the observed radiolytic yield

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of this species,  $G(\text{CuCO}^+) \approx 2 \times 10^{-7} \text{ mol J}^{-1}$ , i.e., 3 reducing equivalents are required to form one CuCO<sup>+</sup>.

After most of the copper is converted into  $CuCO^+$ , the  $\cdot CO_2^-$  radicals will react with this product via reaction 4 or 5.

$$\operatorname{CuCO}^+ + \operatorname{^{\bullet}CO}_2^- \rightarrow \operatorname{Cu(CO)CO}_2$$
 (4)

$$CuCO^{+} + {}^{\bullet}CO_{2}^{-} \rightarrow CO + CuCO_{2}$$
 (5)

The results outlined below suggest that reaction 4 predominates. The adduct undergoes protonation at pH < 4,

$$Cu(CO)CO_2 + H^+ \hookrightarrow Cu(CO)CO_2H^+$$
 (6)

and the product reacts with another CuCO<sup>+</sup>.

$$Cu(CO)CO_{2}H^{+} + CuCO^{+} \rightarrow$$

$$Cu(CO)_{2}^{+} + OH^{-} + Cu^{2+} + CO \quad (7)$$

$$Cu(CO)_{2}^{+} \leftrightarrows CuCO^{+} + CO \quad (8)$$

Under these conditions, where all the initial Cu(II) is already reduced to Cu(I), production of CO requires only two reducing equivalents, in line with the finding that  $G(CO) = 3.3 \times 10^{-7}$  mol J<sup>-1</sup> (i.e., half the total yield of reducing species).

To determine the rate constants of the above reactions, pulse radiolysis experiments were carried out with CO2-saturated aqueous solutions containing CuSO4 and HCO2-/HCO2H at pH 3.4, where  $^{\circ}CO_2^{-}$  is the predominant species formed by the pulse.  $Cu^{2+}$  forms a complex with formate.<sup>18</sup> At 0.1 mol L<sup>-1</sup> formate  $\sim$ 90% of the Cu(II) is present as formate complexes (a mixture of complexes containing 1-4 formate ions). Upon pulse irradiation, Cu(II) is reduced to Cu(I) by the •CO2radicals. The rate constant for reduction of  $Cu_{aq}^{2+}$  by  ${}^{\bullet}CO_2^{-1}$ radicals, measured in the presence of 5 mmol  $L^{-1}$  formate, was  $2 \times 10^9$  L mol<sup>-1</sup> s<sup>-1.10</sup> The rate constant measured at 0.1 mol  $L^{-1}$  formate was lower,<sup>19</sup> 1.5 × 10<sup>8</sup> L mol<sup>-1</sup> s<sup>-1</sup>, and this low value may be ascribed to the Cu(II)-formate complexes (with a contribution from the remaining  $Cu_{aq}^{2+}$ ). On the basis of these rate constants, the reaction of  ${}^{\bullet}CO_2^{-}$  radicals with Cu(II) to form Cu(I) has a half-life  $t_{1/2} < 50 \ \mu s$  at [Cu(II)]  $> 1 \times 10^{-4} \text{ mol}$  $L^{-1}$ . Since Cu(I) reacts with  ${}^{\bullet}CO_2^{-}$  radicals much more rapidly<sup>10</sup> than Cu(II), the accumulated Cu(I) becomes the dominant reactant and forms the adduct (reaction 1). We followed the formation and decay of this adduct at 385 nm (the protonated form at pH 3.4) in consecutive pulses. As observed before under similar conditions,10 the decay of the adduct was rapid in the first several pulses, due to reaction with the remaining Cu(II), but became slower as Cu(II) was progressively reduced to Cu(I). In these experiments, it was not possible to monitor the decay of CuCO<sub>2</sub>H<sup>+</sup> via reaction 3 since a large fraction of the Cu(I) was present as the CuCO<sup>+</sup> complex.

To monitor the spectrum and decay kinetics of the Cu(CO)-CO<sub>2</sub>H<sup>+</sup> adduct in the absence of Cu(II), the solution was irradiated with repetitive pulses until all the Cu(II) was converted into CuCO<sup>+</sup>. The transient spectrum observed by pulse radiolysis of this solution (Figure 5a) has a peak at 385 nm and is ascribed to the Cu(CO)CO<sub>2</sub>H<sup>+</sup> adduct formed via reactions 4 and 6. The molar absorption coefficient of Cu(CO)CO<sub>2</sub>H<sup>+</sup> was calculated to be  $\epsilon_{385} = (1700 \pm 100)$  L mol<sup>-1</sup> cm<sup>-1</sup> by correcting the measured absorbance for the efficiency of reaction of °CO<sub>2</sub><sup>-</sup> with the copper species. The 385 nm peak is similar to that observed before at the same pH at low formate concentrations,<sup>10</sup> which we ascribe to CuCO<sub>2</sub>H<sup>+</sup> formed via reaction 1 and



**Figure 5.** Pulse radiolysis of CO<sub>2</sub>-saturated aqueous solutions containing CuSO<sub>4</sub> and HCO<sub>2</sub>H/HCO<sub>2</sub><sup>-</sup> (0.1 mol L<sup>-1</sup>) at pH 3.4. The solutions were pre-pulsed to convert the Cu<sup>2+</sup> into CuCO<sup>+</sup>; (a) transient absorption spectrum recorded 100  $\mu$  after the pulse, the solution contained 0.1 mmol L<sup>-1</sup> copper; (b) the observed rate of formation at 385 nm as a function of copper concentration, the insert shows a typical trace taken at 0.3 mmol L<sup>-1</sup> copper; (c) decay at 385 nm recorded at 0.3 mmol L<sup>-1</sup> copper, the line was calculated from the model (see text).

subsequent protonation. The present value of  $\epsilon_{385}$ , however, is twice as high as that observed before,<sup>10</sup> suggesting that under the present conditions the adduct is different, possibly indicating that reaction 4 is more important than reaction 5.

The rate of formation of the absorption at 385 nm was determined at various CuCO<sup>+</sup> concentrations, in each case beginning with Cu<sup>2+</sup> and pre-pulsing the solution until all the copper was converted into CuCO<sup>+</sup>. From the concentration dependence shown in Figure 5b we derive a rate constant  $k_4 = (1.5 \pm 0.4) \times 10^8$  L mol<sup>-1</sup> s<sup>-1</sup>. This value is lower than  $k_1$ , which we estimate from our experiments as  $\approx 1 \times 10^9$  L mol<sup>-1</sup>

 $s^{-1}$ . This estimate for  $k_1$  is an order of magnitude lower than that estimated before<sup>10</sup> and the difference may be due to the large difference (20 times) in the formate concentrations used.

The decay of Cu(CO)CO<sub>2</sub>H<sup>+</sup> was followed at several wavelengths at different copper concentrations. The decay traces (an example is shown in Figure 5c) did not fit either first-order or second-order rate law but could be best fitted to a combination of a second-order and a first-order process. A plot of the firstorder rate vs [CuCO<sup>+</sup>] shows a linear dependence from which we derive a rate constant  $k_7 = (5 \pm 2) \times 10^5$  L mol<sup>-1</sup> s<sup>-1</sup>. The plot has a large intercept which may be due to a first-order decomposition of the adduct with  $k \approx 3 \times 10^2 \,\mathrm{s}^{-1}$ . The secondorder component of the kinetic trace leads to an estimated rate constant of  $2k \approx 1 \times 10^8$  L mol<sup>-1</sup> s<sup>-1</sup> for the self-decay of Cu(CO)CO<sub>2</sub>H<sup>+</sup>. The latter reaction is important in the pulse radiolysis experiments, which were done with an initial •CO<sub>2</sub>concentration of (0.7 to 3)  $\times 10^{-5}$  mol L<sup>-1</sup>, but is negligible in the  $\gamma$ -radiolysis experiments, where the steady-state concentration of the radicals is many orders of magnitude lower.

Reaction 1 is the first step in the reduction of  $^{\circ}CO_2^{-}$  radicals by Cu<sup>+</sup> in acidic solutions. A similar reaction may take place with Cu(I) sites in the small copper aggregates, Cu<sub>n</sub><sup>+</sup>. The adduct formed by such a reaction may react with another Cu(I) in solution to form CO. It may be speculated, however, that a Cu(0) site within the same aggregate, if the particle is sufficiently small, may rapidly reduce the adduct before it leaves the particle. Such a reaction is unlikely when the copper particle is large because its reduction potential is much less negative.<sup>11</sup> This is evident from the finding that production of CO stopped when all the copper was in the form of metallic particles.

Finally, experiments were carried out with CO-saturated solutions to test whether CO can be reduced by a similar mechanism as CO<sub>2</sub>. Photolysis of CO-saturated solutions containing acetone, 2-PrOH, PVA, and CuSO<sub>4</sub>, led to production of Cu(0) particles, which were stable after extended photolysis, with no consumption of CO. However, radiolysis of COsaturated solutions of Cu(II) and 2-PrOH led to production of Cu(0) particles and subsequently to a decrease in CO concentration ( $\hat{G} \approx 0.5 \times 10^{-7}$  mol J<sup>-1</sup>). This preferential reduction of the copper ions is in contrast with the radiolytic results in CO<sub>2</sub>saturated solutions and is due to the fact that both the solubility of CO in water and its reactivity toward  $e_{aq}^{-}$  are much lower (factors of 45 and 4.5, respectively) than those of CO<sub>2</sub>. Thus, most solvated electrons and all other reducing radicals produced by the radiolysis react with copper ions leading to production of Cu(0) particles and only when this process is nearly complete

can CO react with  $e_{aq}^{-}$ . Therefore, the reaction between  $^{\circ}CO^{-}$  radicals and Cu(I) cannot be evaluated under these conditions.

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