Stability Constants and Decay of Aqua-Copper(III) – A Study by Pulse Radiolysis with Conductometric and Optical Detection

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Hydroxyl radicals were generated radiolytically in N_2O-saturated aqueous solutions and reacted with Cu^{2+}_{aq} ions. Pulse radiolysis with conductometric detection showed that the aqua-Cu^{III} species thus formed ($k = 3.2 \times 10^8$ dm^3 mol^{-1} s^{-1}) is uncharged at pH 5, i.e. $[Cu(OH)_3]_{aq}$, and from the changes in conductance as a function of pH it has been calculated that $Cu(OH)^{+}_{2aq}$ must have a pK value of 4.8 and $Cu(OH)^{2+}_{aq}$ a value of 3.7. At pH 2.5 there is no strong evidence for the presence of Cu^{3+}_{aq}. Aqua-$Cu(OH)_3$ decays bimolecularly to give Cu^{2+}_{aq} and H_2O_2. $Cu(OH)^{2+}_{aq}$ [and possibly also $Cu(OH)^{+}_{2aq}$] are in equilibrium with Cu^{2+}_{aq} and OH radicals [$K(Cu(OH)^{2+}_{aq}) \approx 3.7 \times 10^4$ dm^3 mol^{-1}]. Rapid electron transfer occurs from Cu^{+}_{aq} to $[Cu(OH)_3]_{aq}$ ($k = 3.5 \times 10^9$ dm^3 mol^{-1} s^{-1}).

Introduction

With the advent of pulse radiolysis in the 1960s it became possible to study the properties of transition-metal ions in unusually high oxidation states, which can be formed in aqueous solutions in reactions with the OH radical. Similarly, their lower than common oxidation states can be generated with the hydrated electron and also by the less-reducing H-atom (for a compilation of rate constants see ref.[1]; for a review see ref.[2]). In the case of Cu^{2+}_{aq} it has been shown that it is reduced at practically diffusion-controlled rates by the hydrated electron and the H-atom.[1] In the latter case a hydride is formed in the first step.[3,4] Even the less reducing superoxide radical ($E^7 = -0.3$ V)[5] is capable of reducing Cu^{2+}_{aq}.[6]

The Cu^{2+}_{aq} ion also reacts with the OH radical, although the rate of this reaction is significantly below diffusion controlled rates [Equation 1, $k_1 \approx 3 \times 10^8$ dm^3 mol^{-1} s^{-1}].[3,7–10] In neutral solution the species formed is characterized by a strong absorption at 280 nm (see Figure 8). From a high-pressure pulse-radiolysis experiment it has been concluded that in the first step a water molecule is replaced by an OH radical [Equation (1)].[10]

$$^{\bullet}OH + Cu(H_2O)^{2+}_n \rightarrow CuOH(H_2O)^{2+}_{n-1} + H_2O \quad (1)$$

Since the rate of build-up is rather slow, the primary species formed in this reaction may subsequently undergo rapid protonation/deprotonation reactions without being noticeable by changes in the UV absorption [Equations (2)–(4)].

$$Cu(H_2O)^{3+}_n \rightleftarrows CuOH(H_2O)^{2+}_{n-1} + H^+ \quad (2)$$

$$CuOH(H_2O)^{2+}_{n-1} \rightleftarrows Cu(OH)_2(H_2O)^{+}_{n-2} + H^+ \quad (3)$$

$$Cu(OH)_2(H_2O)^{+}_{n-2} \rightleftarrows Cu(OH)_3(H_2O)_{n-3} + H^+ \quad (4)$$

Thus, the species that is observed by spectrophotometry does not necessarily carry a doubly-positive charge. The absorption of the aqua-Cu^{III} intermediate varies with pH and from these data it has been deduced that it should have a pK_a value of around 3, a value that has been attributed to equilibrium (2).[3,7] Pulse radiolysis experiments with conductometric detection have indicated, however, that the intermediate observed at around pH 5 might in fact be neutral.[8,11] The rate of decay of the aqua-Cu^{III} intermediate increases with decreasing pH and decreasing Cu^{2+}_{aq} concentration, and below pH 4 no separation between the formation and disappearance was noticed. In addition, there is strong evidence that under these conditions OH radicals and the aqua-Cu^{III} intermediate must be in equilibrium.[3]

There is potentially another kind of Cu^{III} intermediate. When Cu^{+}_{aq} is reacted with H_2O_2 in the presence of methanol, a very effective chain reaction leading to the formation of formaldehyde is induced, but the fact that the chain length strongly depends on the methanol concentration has led to the conclusion that OH radicals are not the chain carrier[12,13] (for ESR experiments and a potentially different interpretation see refs.[14–17]; for the role of such intermediates in DNA cleavage see the review[18]). Because of their strong oxidative power, Cu^{III} complexes have been considered not to play a role in biological systems.[19] However, the presence of Cu^{III} has been postulated in model systems related to enzymes (refs.[20–24]). Interesting data on the properties of Cu^{III}-oligopeptide complexes have been obtained by pulse radiolysis.[25] There are also other means of generating copper(III) and this reagent is of some value in preparative organic chemistry (refs.[26,27]).

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Thus there is some interest in characterising the interesting aqua-Cu^{III} intermediate in more detail. The earlier pulse radiolysis experiments using conductometric detection were carried out in Ar-saturated solutions.[8] This is not the best condition for such an experiment. In the radiolysis of water [Equation (5)] OH radicals, hydrated electrons and H atoms are formed side by side [$G(^{\bullet}OH) \approx G(e^-_{aq}) \approx 2.8 \times 10^{-7}$ mol J^{-1}, $G(H^{\bullet}) \approx 0.6 \times 10^{-7}$ mol J^{-1}, $G(H_2O_2) = 0.7 \times 10^{-7}$ mol J^{-1}, $G(H_2) = 0.5 \times 10^{-7}$ mol J^{-1}].[28] Thus, in assessing the state of charge of the intermediate in question, the observed conductance changes have to be corrected for contributions caused by the reduction processes (formation of Cu^+_{aq} and H^+). Their assignment to $[Cu(OH)_3]_{aq}$ has been supported by a more decisive experiment.[11] In fact, such a correction can be largely avoided by saturating the solutions with nitrous oxide, which converts the hydrated electron into an OH radical [Equation (6); $k_6 = 9.7 \times 10^9$ dm^3 mol^{-1} s^{-1}].[1] Under these conditions a correction for a contribution of the H atom is minor (ca. 10%), at least when the pH is not too low, [Equation (7)], $k_7 = 2.3 \times 10^{10}$ dm^3 mol^{-1} s^{-1}.

$$H_2O \xrightarrow{\text{ionizing radiation}} {}^{\bullet}OH, e^-_{aq}, H^{\bullet}, H^+, H_2O_2, H_2 \quad (5)$$

$$e^-_{aq} + N_2O \rightarrow {}^{\bullet}OH + N_2 + OH^- \quad (6)$$

$$e^-_{aq} + H^+ \rightarrow H^{\bullet} \quad (7)$$

We have again used this approach to study the pH dependence of the stability constants of the aqua-Cu^{III} intermediates over a wide pH range (pH 2.5–5). Moreover, it will be shown that differently charged aqua-Cu^{III} may decay by different routes. Indeed, at low pH reaction (1) becomes reversible.

Results and Discussion

Determination of Stability Constants

Conductometric experiments have to be carried out at pH $\leq$ 5 in order to avoid buffering effects of Cu^{2+}_{aq} [p$K(Cu^{2+}_{aq}) \approx$ 7.2].[29] Low Cu^{2+}_{aq} concentrations have to be used in order to ensure that their reaction with the hydrated electron [$k(e^-_{aq} + Cu^{2+}_{aq} \rightarrow Cu^+_{aq}) \approx 3 \times 10^{10}$ dm^3 mol^{-1} s^{-1}][1] does not compete significantly with reaction (6). At these low Cu^{2+}_{aq} concentrations the rate of the reaction of the OH radical with Cu^{2+}_{aq} is rather slow, and very low doses per pulse (e.g. 1 $\leq$ Gy, Figure 1) have to be applied for a quantitative reaction because of the fast recombination of the OH radicals [2 $^{\bullet}OH \rightarrow H_2O_2$; $2k = 5.5 \times 10^9$ dm^3 mol^{-1} s^{-1}].[1] The conductance signal is even further reduced at high doses, since proton formation will lower the pH, an effect that also leads to a decrease in the conductance signal (cf. Figure 3).

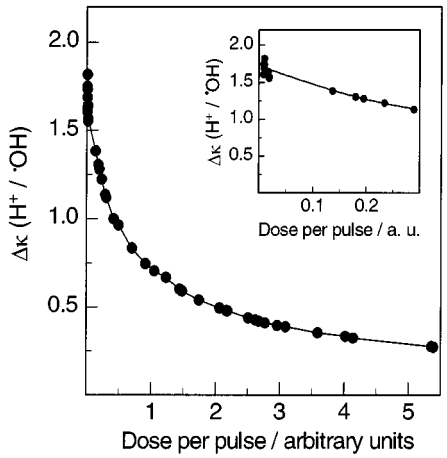

Figure 1. Pulse radiolysis of N_2O-saturated solutions of Cu^{2+}_{aq} (1×10^{-4} mol dm^{-3}), pH 5.0. The yields of conductance change (number of H^+ released per $^{\bullet}OH$ reacted) as a function of dose per pulse. One arbitrary dosimeter unit (a. u.) is approximately equivalent to 12 Gy

When the reaction of OH radicals under such conditions is followed by conductometry, the rate of increase in the conductance is proportional to the Cu^{2+}_{aq} concentration (Figure 2). From the slope of the straight line in Figure 2, a rate constant of 3.2×10^8 dm^3 mol^{-1} s^{-1} is calculated for the reaction of OH radicals with Cu^{2+}_{aq}, which compares well with the literature data obtained by optical detection (see above).

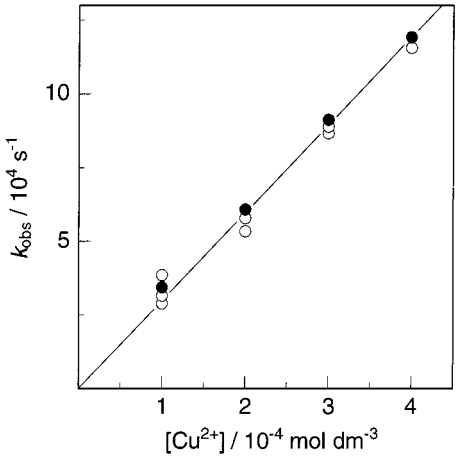

Figure 2. Pulse radiolysis of N_2O-saturated solutions of Cu^{2+}_{aq}. The rate of absorbance change at 350 nm (●; pH 5, extrapolation to zero dose) and conductance changes (○; pH 4, dose per pulse $\leq$ 1 Gy) as a function of the Cu^{2+}_{aq} concentration

In Figure 3 the proton yield per OH radical is plotted as a function of pH. These values are based upon dimethyl sulfoxide dosimetry, where one mol of OH radicals yields close to one mol of methanesulfinic acid.[30] It can be calculated from the data shown in Figure 3 that at pH 5 two mol of protons are formed per mol of OH radical reacted, i.e. the resulting aqua-Cu^{III} species must be uncharged $[Cu(OH)_3]_{aq}$, see Equation (8), which is in agreement with the earlier[8,11] conclusion.

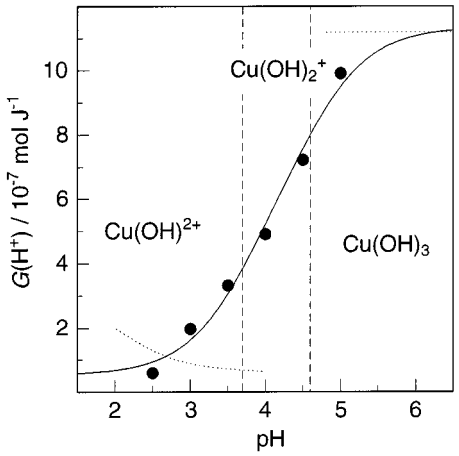

Figure 3. Pulse radiolysis of N_2O-saturated solutions of Cu^{2+}_{aq} (1×10^{-4} mol dm^{-3}). Conductance changes as a function of pH. Values extrapolated to zero dose per pulse

$$Cu^{2+}_{aq} + {}^{\bullet}OH + 2\,H_2O \rightarrow [Cu(OH)_3]_{aq} + 2\,H^+ \quad (8)$$

$$Cu^{2+}_{aq} + {}^{\bullet}OH + H_2O \rightarrow Cu(OH)^{+}_{2\,aq} + H^+ \quad (9)$$

$$Cu^{2+}_{aq} + {}^{\bullet}OH \leftrightharpoons Cu(OH)^{2+}_{aq} \quad (10)$$

Upon lowering the pH the proton yield drops, and at pH 2.5 no protons are liberated beyond those formed by the H atom with Cu^{2+}_{aq} ($Cu^{2+}_{aq} + H^{\bullet} \rightarrow Cu^{+}_{aq} + H^+$; note the dashed line in Figure 3). The experimental value at pH 2.5 is somewhat lower than this limit, which might suggest the onset of Cu^{3+}_{aq} formation. However, the relatively high background conductivity of the solution at this pH along with the low signals make the measurement conditions unfavourable. Thus, no firm conclusions can be drawn regarding the presence of the triply-charged species.

The pH range where this decrease is observed is rather narrow, although two pK values must be involved [Equations (3) and (4)].

The data can be fitted (solid line in Figure 3) using pK values at pH = 3.7 and 4.6. Our observations are in agreement with the earlier conclusion[8,11] that at pH 5 the aqua-Cu^{III} species are largely uncharged. The mono-charged species only dominates at around pH 4. In the more acidic pH range the aqua-Cu^{III} is doubly-charged and, as mentioned above, evidence for a triply-charged species at pH $\leq$ 2.5 is very weak. The difference between our results and those reported by Asmus et al.[11] only concerns the strongly acidic range. In the earlier study[11] a ten-fold higher Cu^{2+}_{aq} concentration was used and this, together with the protons, competes with N_2O for the solvated electrons. The reactions of Cu^{2+}_{aq} with the solvated electron and the H atom lead to the formation of Cu^{+}_{aq} and a proton. The reported data were corrected, but it is not stated whether the correction was only for the reduction in OH-radical yield or whether the latter effect was also corrected for in the evaluation of the conductance signals.

It is noted that the aqua-Cu^{III} species deprotonates only at much lower pH values than Cu^{2+}_{aq} (Cu^{2+}_{aq} dominates below pH 7).

A comparison can be made between the aqua-Cu^{III} and the isoelectronic aqua-Pd^{II} complex. The pK_a value of the $[Pd(H_2O)_3OH]^+$ species has been recently re-measured[31] as being close to 3.0 and the pK_a value of the neutral species must be even higher (not measurable because of the formation of polynuclear complexes). In this case the pK_a value of aqua-$Cu(OH)^{+}_{2}$ (equivalent to the neutral aqua-Pd^{II} complex) has been found at 3.7. This pK_a value is not unexpected given that the aqua-Cu^{III} ion is slightly smaller. The structure of aqua-Pd^{II} is square planar,[32] and one may therefore expect that the analogous aqua-Cu^{III} species has the same structure.

Decay of Aqua-Copper(III)

Aqua-$Cu(OH)_3$ is a highly reactive species. It decays under our experimental conditions on the millisecond time range and leads to restoration of the original conductance (Figure 4).

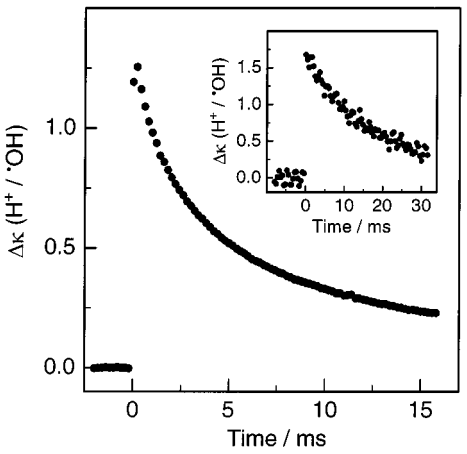

Figure 4. Pulse radiolysis of N_2O-saturated aqueous solutions of Cu^{2+}_{aq} (1×10^{-4} mol dm^{-3}) at pH 5 and a dose of 2.2 Gy (Inset: 0.1 Gy). Decay of aqua-$Cu(OH)_3$ as followed by conductance changes

At pH 5 the decay is largely bimolecular, i.e. the first half-life of decay decreases with increasing aqua-$Cu(OH)_3$ concentration. To achieve this by increasing the dose per pulse is not easy because of the slowness of the reaction of the OH radical with Cu^{2+}_{aq} (see Figure 1). However, the relevant aqua-$Cu(OH)_3$ concentration can be calculated from its maximum absorbance at 270 nm (Figure 5). These data yield a bimolecular rate constant of 1.8×10^8 dm^3 mol^{-1} s^{-1}. Similar experiments have been performed using conductometric detection. Although the dose per pulse was not known precisely in the experiments shown in the inset of Figure 5 (the estimated error is ±20%; for a possible method to determine this value exactly see ref.[33]), the approximate rate constant for the bimolecular decay of aqua-$Cu(OH)_3$ calculated from these data is $2k = 2 \times 10^8$ dm^3 mol^{-1} s^{-1}. These two sets of data agree well, but are considerably higher than the value of 4.6×10^7 dm^3 mol^{-1} s^{-1} reported earlier.[3]

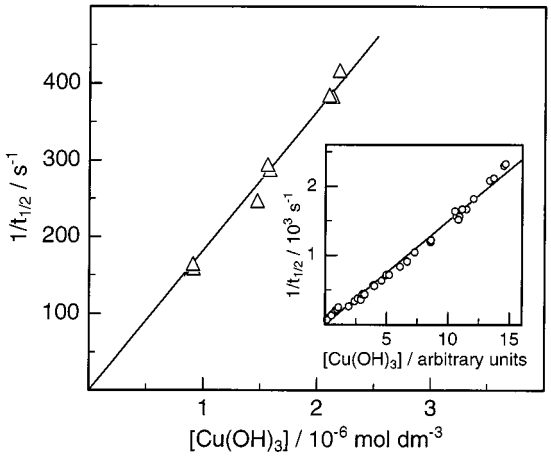

Figure 5. Pulse radiolysis of N_2O-saturated aqueous solutions of Cu^{2+}_{aq} (2×10^{-4} mol dm^{-3}) at pH 5. The reciprocal first half-lives of the decay of aqua-Cu(OH)$_3$ at 270 nm as a function of the initial $[Cu(OH)_3]_{aq}$ concentration (see text). Inset: Conductivity measurements; the initial [aqua-Cu(OH)$_3$] was taken to be proportional to the $[H^+]$ 100 μs after the pulse

It is reasonable to assume that in this bimolecular decay two Cu^{2+}_{aq} ions are reformed and one mol of H_2O_2 is thereby produced [Equation (11)].

$$2\,[Cu(OH)_3]_{aq} \rightarrow 2\,Cu^{2+}_{aq} + 4\,OH^- + H_2O_2 \quad (11)$$

This stoichiometry is indeed observed when a series of pulses of 1 Gy is given to an N_2O-saturated solution of Cu^{2+}_{aq} (2×10^{-4} mol dm^{-3}). Under these conditions the H_2O_2 concentration increases linearly with increasing dose (data not shown), and from these data a value of $G(H_2O_2) = 2.6 \times 10^{-7}$ mol J^{-1} is calculated. This value is not too far from that expected considering that Cu^{+}_{aq} [$G(Cu^{+}_{aq}) \approx 0.7 \times 10^{-7}$ mol J^{-1} under these conditions] will react rapidly with aqua-Cu(OH)$_3$ (see below) and thus will prevent the formation of H_2O_2. However, when the same experiment is carried out at the low dose rates of γ-radiolysis, only $G(H_2O_2) = 0.5 \times 10^{-7}$ mol J^{-1} is measured. Thus, reactions that consume the H_2O_2 formed must play a role in this situation and these are discussed below.

The rate of disappearance of the aqua-Cu^{III} intermediates is pH-dependent and increases as the solutions become more acidic. In addition, at low pH, build-up and decay were not clearly distinguishable.[3] It has been concluded that during this decay OH radicals are liberated [Equation (10)].[3]

A considerable drawback in the determination of equilibrium (10) by UV spectrophotometry is the fact that the reported[3,7] spectrum of the OH radical is very close to that resulting from its reaction with Cu^{2+}_{aq} at low pH. Moreover, at these low absorptions (cf. Figure 9) the signals become very noisy at the low doses required. This prevents the determination of equilibrium (10) by optical detection. However, conductometric experiments may allow some firmer conclusions to be drawn. In order to test the liberation of OH radicals, trace amounts (10^{-6} mol dm^{-3}) of dimethyl sulfoxide were added [Equation (12); $k_{12} = 7 \times 10^9$ dm^3 mol^{-1} s^{-1}].[30]

$$^{\bullet}OH + (CH_3)_2SO \rightarrow CH_3S(O)O^- + H^+ + {}^{\bullet}CH_3 \quad (12)$$

This reaction leads to the formation of methanesulfinic acid and hence contributes to a small extent to the observed conductance changes that occur immediately after the pulse, since these small amounts only scavenge ca. 9% of the primary OH radicals. However, the competition between Cu^{2+}_{aq} and dimethyl sulfoxide can become much more favourable for dimethyl sulfoxide in the long run. This is due to the fact that OH radicals liberated from the aqua-Cu^{III} intermediates will then have a chance to react with dimethyl sulfoxide in competition with a reaction with Cu^{2+}_{aq} that restores the aqua-Cu^{III} species [see Equation (10)].

This system was first tested at pH 5, where it has been shown above that very few, if any, OH radicals are liberated on the time scale of the decay of aqua-Cu(OH)$_3$, which dominates at this pH. If OH radicals had been eliminated, the conductance signal should have dropped during the bimolecular decay from two H^+ per OH radical to one H^+ per OH radical (dashed line in Figure 6). However, the former level of conductance is fully restored, confirming the above conclusions that at pH 5 no OH radicals are liberated on the pulse radiolysis time scale.

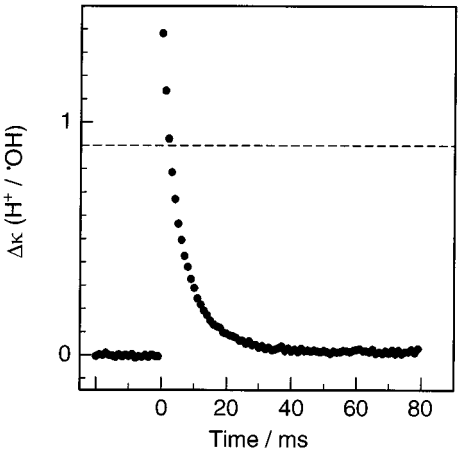

Figure 6. Pulse radiolysis of N_2O-saturated aqueous solutions of Cu^{2+}_{aq} (2×10^{-4} mol dm^{-3}) at pH 5 in the presence of dimethyl sulfoxide (10^{-6} mol dm^{-3}). The dashed line indicates the conductance change that should have been reached if aqua-Cu(OH)$_3$ had released an OH radical and the OH radicals had reacted with dimethyl sulfoxide

However, at pH 2.5, where no conductance changes are observed upon the reaction of OH radicals with Cu^{2+}_{aq}, the conductance should increase to a value of one H^+ per OH radical during the decay of the aqua-Cu^{III} intermediate when the released OH radical is scavenged by dimethyl sulfoxide. This limiting value is indicated by the dashed line in Figure 7.

From the data shown in Figure 7 it is possible to estimate the stability constant K_{10} by a simulation of the reactions that must contribute (yields of H atoms and OH radicals in N_2O-saturated solutions at this low pH [$G(H^{\bullet}) = 1.2 \times 10^{-7}$ mol J^{-1}, $G(^{\bullet}OH) = 5.0 \times 10^{-7}$ mol J^{-1}], formation of Cu^{+}_{aq}

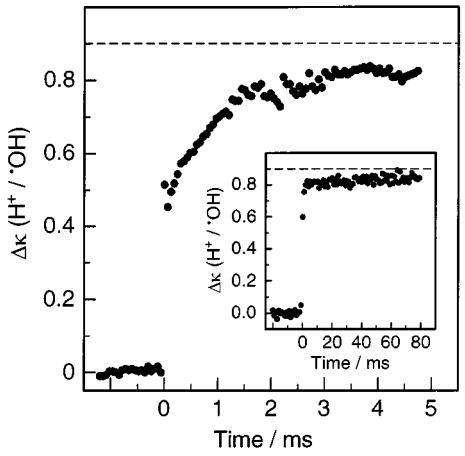

Figure 7. Pulse radiolysis of N_2O-saturated aqueous solutions of Cu^{2+}_{aq} (2×10^{-4} mol dm^{-3}) at pH 2.5 in the presence of dimethyl sulfoxide (10^{-6} mol dm^{-3}). The dashed line indicates the conductance change that should have been reached if the aqua-$Cu(OH)^{2+}$ had released an OH radical and the OH radicals had reacted with dimethyl sulfoxide

and H^+ by the H atom, bimolecular decay of Cu^+_{aq} and $Cu(OH)^{2+}_{aq}$, see below) to the observed conductivity changes, although practically no experimental variations can be made to put this value on a better footing. The experimental data are reasonably modelled by taking $k_{10} \approx 8 \times 10^3$ s^{-1}, $k_{-10} = 3 \times 10^8$ dm^3 mol^{-1} s^{-1}, i.e. $K_{10} \approx 3.7 \times 10^4$ dm^3 mol^{-1}. This value is of the same order as the values reported earlier ($K = 1.1 \times 10^4$ dm^3 mol^{-1}; at pH 3.65).[3]

The fact that OH radicals can be liberated in unimolecular reactions of aqua-Cu^{III} intermediates allows us to interpret the observation that at the low dose rates of γ-radiolysis, where reactions that are kinetically of first order will dominate, no H_2O_2 is formed at pH 2.5 and only low yields are formed at pH 5 (see above). The hydroxyl radical reacts with H_2O_2 by H-abstraction [Equation (13), $k_{13} = 2.7 \times 10^7$ dm^3 mol^{-1} s^{-1}][1] and this reaction yields the superoxide radical, which, although a peroxyl radical, is a powerful reductant[34] and readily reacts even with Cu^{2+}_{aq} [Equation (14)].[6]

$$^{\bullet}OH + H_2O_2 \rightarrow H_2O + HO^{\bullet}_2 \quad [HO^{\bullet}_2 \leftrightarrows O^{\bullet}_2{}^- + H^+;\ pK_a(HO^{\bullet}_2) = 4.8] \qquad (13)$$

$$Cu^{2+}_{aq} + O^{\bullet}_2{}^- \rightarrow Cu^+_{aq} + O_2 \qquad (14)$$

At pH 5 and with low dose rates of γ-radiolysis the yield of H_2O_2 was considerably lower than the value obtained under the high dose rate conditions of electron beam irradiation. Thus, at this pH some OH radicals must also have been liberated during the bimolecular decay of the aqua-Cu^{III} intermediates. It is hence concluded that either aqua-$Cu(OH)_3$ itself or aqua-$Cu(OH)^+_2$/aqua-$Cu(OH)^{2+}$, which are also present in lower steady-state concentrations, can liberate OH radicals [aqua-$Cu(OH)_3$ – albeit very slowly, if at all, see above].

Reaction of Aqua-$Cu(OH)_3$ with Cu^+_{aq}

In order to determine the rate of the reaction of aqua-$Cu(OH)_3$ with Cu^+_{aq} [Equation (15)] conditions were chosen where $O^{\bullet}_2{}^-$ (i.e. Cu^+_{aq}) is in a large excess in comparison with aqua-$Cu(OH)_3$. This situation can be achieved by pulse-irradiation of O_2-saturated solutions of Cu^{2+}_{aq} (1×10^{-3} mol dm^{-3}) that also contain formate ions (1×10^{-3} mol dm^{-3}). Under these conditions the OH radicals will be partially scavenged by formate [Equation (16)] and the resulting $CO^{\bullet}_2{}^-$ radicals converted by O_2 into $O^{\bullet}_2{}^-$ radicals [Equation (17)]. In addition, the solvated electrons are also converted by O_2 into $O^{\bullet}_2{}^-$ radicals, and some of the solvated electrons will also contribute to the Cu^+_{aq} yield [Equations (18) and (19)].

$$Cu^+_{aq} + [Cu(OH)_3]_{aq} \rightarrow 2\,Cu^{2+}_{aq} + 3\,OH^- \qquad (15)$$

$$^{\bullet}OH + HCO^-_3 \rightarrow H_2O + CO^{\bullet}_2{}^- \qquad (16)$$

$$CO^{\bullet}_2{}^- + O_2 \rightarrow CO_2 + O^{\bullet}_2{}^- \qquad (17)$$

$$e^-_{aq} + O_2 \rightarrow O^{\bullet}_2{}^- \qquad (18)$$

$$e^-_{aq} + Cu^{2+}_{aq} \rightarrow Cu^+_{aq} \qquad (19)$$

Under such conditions, the decay kinetics of aqua-$Cu(OH)_3$ are of (pseudo) first order. By increasing the dose per pulse, the Cu^+_{aq} concentration is raised correspondingly, and from the linear k_{obs} vs. Cu^+_{aq} concentration relationship (Figure 8) a value of $k_{15} = 3.5 \times 10^9$ dm^3 mol^{-1} s^{-1} is calculated. Thus, the expectation discussed above, namely that aqua-Cu^{III} intermediates are readily reduced by Cu^+_{aq}, has been substantiated.

In the experiments represented in Figure 8 the decay of aqua-$Cu(OH)_3$ was followed by optical detection. This required a re-determination of the absorption spectrum of aqua-$[Cu(OH)_3]_{aq}$, which is shown in Figure 9. In the present study much lower doses per pulse were used than was possible in the earlier[7] study.

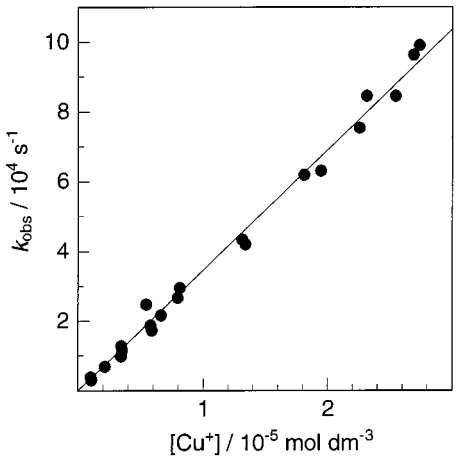

Figure 8. Pulse radiolysis of O_2-saturated aqueous solutions of Cu^{2+}_{aq} (1×10^{-3} mol dm^{-3}) containing 1×10^{-3} mol dm^{-3} of formate, pH 5.0. The observed pseudo-first-order rate constant of aqua-$Cu(OH)_3$ decay, followed as absorbance decrease at $\lambda = 300$ nm, as a function of Cu^+_{aq} concentration

It can be seen from Figure 9 that there is a considerable drop in absorbance with decreasing pH. Taking the pK

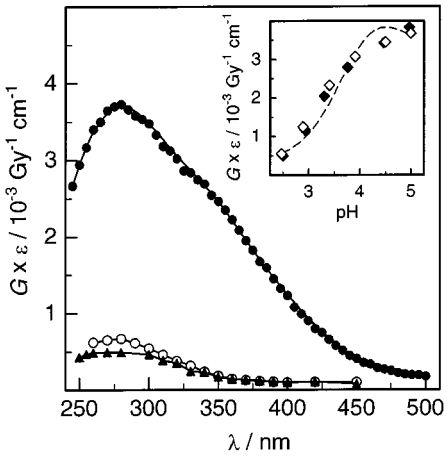

Figure 9. Pulse radiolysis of aqueous solutions of Cu^{2+}_{aq} (2×10^{-4} mol dm^{-3}). Absorption spectra (in units of $G \times \varepsilon$) recorded at 60–80 μs after a pulse of 1.8 Gy. Filled circle: N_2O-saturated solutions of pH 5.0; open circle: N_2O-saturated, pH 2.5; filled triangle: Ar-saturated, pH 2.5. Inset: Absorbance at 270 nm (in units of $G \times \varepsilon$) as a function of pH; filled square: $Cu(SO_4)/H_2SO_4$; open square: $Cu(ClO_4)_2/HClO_4$

values that were determined earlier and fixing the absorption coefficient of $Cu(OH)^{2+}_{aq}$ at 500 dm^3 mol^{-1} cm^{-1} (i.e. close to that of the OH radical),[1] the best fit (dashed line in the inset of Figure 9) is obtained with $\varepsilon[Cu(OH)^{+}_{2\,aq}] = 8000$ dm^3 mol^{-1} cm^{-1} and ε[aqua-$Cu(OH)_3$] = 4800 dm^3 mol^{-1} cm^{-1}. The reason why the monocharged species has the highest absorption coefficient is not yet understood. In the inset in Figure 9are shown the data obtained with copper sulfate and copper perchlorate. This is a strong indication that the anion has no influence on the absorption spectra (see also ref.[3]), in particular the strong absorptions of the neutral and the monocharged species are not due to complexation by the sulfate ion.

Some experiments were also performed at pH 2.5 in Ar-saturated solutions (see filled triangle in Figure 9). Under these conditions approximately equal amounts of aqua-$Cu(OH)^{2+}$ and Cu^{+}_{aq} are formed (note the conversion of the solvated electron into an H atom at low pH). The experiments show that Cu^{+}_{aq} also absorbs in this wavelength region, but its contribution to the spectrum obtained in N_2O-saturated solutions (see open circle in Figure 9) is only small.

Experimental Section

Copper(II) sulfate pentahydrate, copper(II) perchlorate and all other chemicals were used as received. Solutions were made up in Milli-Q-filtered water (Millipore). The pH was adjusted with H_2SO_4 or with $HClO_4$. Prior to irradiation, solutions were saturated for 45 min with N_2O, which had been purified using an Oxisorb column (Messer-Griesheim), or for 20 min with O_2. γ-Irradiation was performed with a panorama ^{60}Co-γ-source (Nuclear Engineering) at a dose rate of 0.67 Gy s^{-1}. Pulse radiolysis measurements were carried out with a van de Graaff accelerator, generating 0.4 μs pulses of 2.8 MeV electrons. Details of the conductometric and optical detection systems are given elsewhere.[35,36] Dimethyl sulfoxide and thiocyanate were used as dosimeters for the conductometric and optical pulse radiolysis experiments.[30,37] In the conductometric experiments dosimetry allows the calculation of the yields (G value) of the conducting species formed, although their absolute concentrations cannot be ascertained by this method. The knowledge of the absolute concentration is only required for the evaluation of bimolecular rate constants. In principle this can be determined,[33] but for the present work it was sufficient to know the approximate valus for dose per pulse (± 20%). One dosimeter unit, as given in the figures, corresponds to approximately 12 Gy.

For the determination of H_2O_2 yields (measured spectrophotometrically with titanyl sulfate)[38] under pulse-irradiation conditions, solutions contained in a small vessel that permitted continuous N_2O-saturation were subjected to a series of electron pulses. The absorbed dose was determined using the O_2-saturated Fricke dosimeter.

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