tendency for racemic adsorption. In fact, both enantiomeric and racemic $[Co(en)_3]^{3+}$ are adsorbed, occupying three cation-exchange sites per chelate.[17]

The resolution of $Fe(phen)_2(CN)_2$ at the expense of Λ-$[Ni(phen)_3]^{2+}$ (Table IV) shows promise for the use of a clay as a material for optical resolution. Although column chromatography was impossible in the present systems, other chiral complexes like $Co(acac)_3$ (acac ≡ acetylacetonato) are actually resolved on a Δ-$[Ni(phen)_3]^{2+}$–montmorillonite column.[18,19]

Registry No. $Fe(phen)_2(CN)_2$, racemic, 15362-08-0; Λ-$Fe(phen)_2(CN)_2$, 30872-77-6; Δ-$Fe(phen)_2(CN)_2$, 80875-80-5; $Fe(bpy)_2(CN)_2$, racemic, 29013-61-4; Δ-$Fe(bpy)_2(CN)_2$, 55101-89-8; (Na^+M^-), 1318-93-0; Λ-$[Ni(phen)_3]$[bis(antimonous *d*-tartrate)], 80822-39-5; Δ-$[Ni(phen)_3][ClO_4]_2$, 14282-09-8.

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Properties of Copper(II) Hydride Formed in the Reaction of Aquacopper(I) Ions with Hydrogen Atoms. A Pulse Radiolytic Study[1]

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The spectrum of $Cu{-}H^+(aq)$, formed via $Cu^+ + H \rightarrow Cu{-}H^+(aq)$ in aqueous solutions, is reported. In neutral solutions it decomposes via $Cu{-}H^+(aq) + H_2O \rightarrow Cu^{2+}(aq) + H_2 + OH^-(aq)$ with a rate of $4 \times 10^3\ s^{-1}$. The properties of $Cu{-}H^+(aq)$ are discussed and compared with those of similar $Cu^{II}{-}R$ compounds.

The formation of $CuH^+(aq)$ ions as intermediates in catalytic reductions by hydrogen in the presence of copper(II) ions was proposed long ago.[3] The mechanism of formation of $CuH^+(aq)$ was suggested to be

$$Cu^{2+}(aq) + H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cu{-}H^+(aq) + H_3O^+(aq) \qquad (1)$$

$$k_1 = 9.5 \times 10^{-5}\ M^{-1}\ s^{-1} \text{ at } 110\ °C$$

where this reaction is followed, in the absence of other oxidants, by[3]

$$Cu{-}H^+(aq) + Cu^{2+}(aq) \rightarrow 2Cu^+(aq) + H_3O^+(aq) \qquad (2)$$

We decided to try to study, using the pulse radiolytic technique, the properties of $Cu{-}H^+(aq)$ by following the reaction

$$H + Cu^+(aq) \rightarrow Cu{-}H^+(aq) \qquad (3)$$

in parallel to the reactions

$$\cdot RH + Cu^+(aq) \rightarrow Cu{-}RH^+(aq) \qquad (4)$$

which were recently observed.[4–7] Some of the latter reactions were suggested to be equilibrium processes.[4,5]

Recently, Ferraudi reported the observation of $CuHCl_3^{2-}$ formed via an analogous mechanism in the photolysis of $CuCl_3^{2-}$.[8] $HCuCl_3^{2-}$, $HCuCl_2^-$, $HCu_2Cl_3^-$, or similar complexes have also been shown to be intermediates in the production of hydrogen from the UV photolysis of chlorocuprate(I) ions.[8b] It is of interest to compare the properties of $Cu{-}H^+(aq)$ with those of $CuHCl_3^{2-}$.

Experimental Section

Deaerated solutions containing $(2–10) \times 10^{-4}$ M $CuSO_4$ at pH 3.2–6.0 were irradiated by short pulses from the electron linear accelerator at Argonne National Laboratory. The solutions were irradiated in Suprasil cells which were contained in specially designed high-pressure cells.[9] After deaeration the solutions were always saturated with hydrogen, usually at 100 atm pressure, and for blank experiments, at atmospheric pressure. No observable reaction between Cu^{2+} and H_2 occurs under these conditions at room temperatures within several hours.

The spectra of the transients were recorded with use of the streak camera;[10] i.e., the total spectrum was recorded at desired times with application of a single pulse. The kinetics of reaction were followed with the regular photomultiplier setup.[11]

Dosimetry was carried out by measuring the yield of $(NCS)_2^{-}\cdot$ at 475 nm formed by identical pulses in the same cells containing N_2O-saturated solutions of 1×10^{-3} M NaNCS.[11]

Results and Discussion

The radiolysis of water or dilute aqueous solutions may be summed up by[12]

$$H_2O \rightarrow e_{aq}^-, H, OH, H_2O_2, H_2, H_3O^+(aq), OH^-(aq) \qquad (5)$$

where the yields, G, of these primary products are $G_{e_{aq}^-} = 2.65$, $G_H = 0.60$, $G_{OH} = 2.65$, $G_{H_2O_2} = 0.75$, $G_{H_2} = 0.45$, $G_{H_3O^+} = 3.65$, and $G_{OH^-(aq)} = 1.00$ in units of molecules per 100 eV absorbed in the solution.[12]

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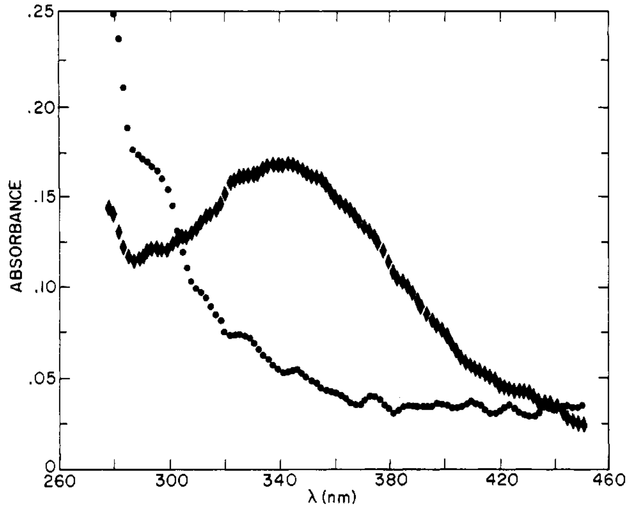

Figure 1. Spectra obtained with use of the streak camera, with solution composition 5 × 10^{-4} M $CuSO_4$ saturated with 100 atm H_2 at pH 5.6. Pulse intensity yielded a total free radical concentration of 3.3 × 10^{-4} M. (◆) spectrum immediately after a 3-μs pulse and (●) spectrum 150 μs after the pulse.

In hydrogen-saturated, neutral or slightly acidic solutions containing $CuSO_4$ the secondary reactions (6)–(13) have to

$$e_{aq}^- + Cu^{2+}(aq) \rightarrow Cu^+(aq) \quad k = 3 \times 10^{10}\ M^{-1}\ s^{-1\,13} \tag{6}$$

$$e_{aq}^- + H_3O^+(aq) \rightarrow H \qquad k = 2.2 \times 10^{10}\ M^{-1}\ s^{-1\,13} \tag{7}$$

$$e_{aq}^- + Cu^+(aq) \rightarrow Cu^0(aq) \qquad k \text{ unknown} \tag{8}$$

$$OH + Cu^{2+}(aq) \rightarrow Cu^{III}(aq) \quad k = 3.1 \times 10^8\ M^{-1}\ s^{-1\,14} \tag{9}$$

$$OH + H_2 \rightarrow H + H_2O \qquad k = 4.5 \times 10^7\ M^{-1}\ s^{-1\,14} \tag{10}$$

$$H + Cu^{2+}(aq) \rightarrow Cu^+(aq) + H_3O^+(aq) \quad k \leq 1 \times 10^6\ M^{-1}\ s^{-1\,4,15} \tag{11}$$

$$H + H \rightarrow H_2 \qquad k = 1.3 \times 10^{10}\ M^{-1}\ s^{-1\,15} \tag{12}$$

$$H + Cu\text{-}H^+(aq) \rightarrow Cu^+ + H_2 \tag{13}$$

be considered, along with reactions 1, 2, and 3. Radical–radical reactions of e_{aq}^- and OH are not included in this list as the concentrations of $Cu^{2+}(aq)$, $H_3O^+(aq)$, and H_2 are high enough, and thus their contribution is negligible relative to reactions 6–10. Reactions 3 and 13 were not observed up to the present study.

When neutral solutions containing (2–10) × 10^{-4} M $CuSO_4$ saturated with 100 atm H_2 were irradiated, the formation of unstable products absorbing in the near-UV was observed. The spectra observed at 3 and 150 μs after the pulse are plotted in Figure 1. It should be noted that the spectrum observed at 3 μs after the pulse differs from that of $Cu^+(aq)$[16] and $Cu^{III}(aq)$.[17] When identical solutions saturated under only 1 atm H_2 were irradiated, the spectrum of the intermediate observed was identical with that of $Cu^{III}(aq)$, i.e., λ_{max} = 290 nm in accordance with expectation, if we take into account reactions 1–12 and remember that in the wavelength range studied $\epsilon(Cu^{III}(aq)) >> \epsilon(Cu^+(aq))$. The spectrum 150 μs after the pulse, Figure 1, is attributed to $Cu^+(aq)$.[17]

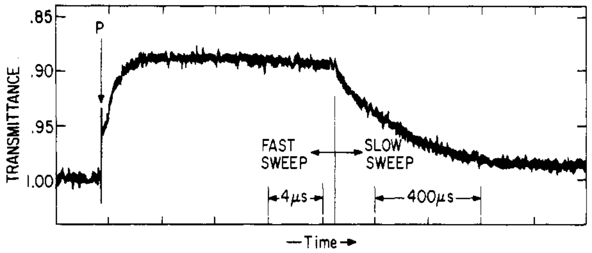

Figure 2. Kinetic spectrophotometric trace of a pulse-radiolyzed solution of 1 × 10^{-3} M $CuSO_4$ saturated with 100 atm H_2 at pH 5.6 and measured at 340 nm. *P* denotes time at which the 40-ns pulse, producing 4 × 10^{-5} M free radicals, entered the solution.

Under the experimental conditions all the e_{aq}^- are transformed into $Cu^+(aq)$ and H atoms via reactions 6 and 7. At the lowest $Cu^{2+}(aq)$ concentration used $t_{1/2}(e_{aq}^-) \leq$ 100 ns. The spike of absorption observed when the pulse is delivered, shown in Figure 2, is due to the absorption of e_{aq}^-. On repetitive pulses the concentration of $Cu^+(aq)$ increases and that of $Cu^{2+}(aq)$ decreases. As a result reaction 8 competes with reaction 6, and indeed the precipitation of Cu^0 formed via reaction 8 was observed upon repetitive pulses.[18] Over 95% of the OH radicals are transformed into H atoms via reaction 10; the rest forms $Cu^{III}(aq)$ via reaction 9 (under 100 atm H_2 the yield of $Cu^{III}(aq)$ is less than 5% even when $[Cu^{2+}(aq)]$ = 1 × 10^{-3} M). When the pressure is reduced to 1 atm, reaction 9 becomes the dominant one, and indeed the formation of $Cu^{III}(aq)$ is observed (see above). At 100 atm H_2 the half-life of the OH radicals is less than 150 ns. The rate of formation of the transient absorbing at 340 nm corresponds to a half-life of 700–3500 ns, depending on the pulse intensity (see below). Thus the formation of the transient absorbing at 340 nm cannot be due to a direct reaction of e_{aq}^- or OH and has to be due to a reaction of the secondary products formed, $Cu^+(aq)$ and/or H atoms. The reaction of H atoms with $Cu^{2+}(aq)$, reaction 11, is too slow to account for the formation of the transient; furthermore, the latter rate is independent of $[Cu^{2+}(aq)]$. The transient also cannot be due to a reaction of $Cu^+(aq)$ with H_2 as those are the final products in the studied system or to a reaction of $Cu^+(aq)$ with $Cu^{2+}(aq)$. We suggest therefore that the transient formed after several microseconds is $Cu\text{-}H^+(aq)$ via reaction 3. The kinetics of formation of $Cu\text{-}H^+(aq)$ were followed at 340 nm (Figure 2). The rate observed varied between 2 × 10^5 and 1 × 10^6 s^{-1}, depending on the pulse intensity. The lower rate corresponds to $[H]^0 + [Cu^+]^0 \approx 5$ μM whereas the higher rate was observed when $[H]^0 + [Cu^+]^0 \approx 40$ μM. Computer simulations yield $5 \times 10^9 \leq k_3 \leq 2 \times 10^{10}$ M^{-1} s^{-1}; the rate of formation clearly includes a large contribution of reaction 12, however, toward the end of the formation reaction $[Cu^+] > [H]$, and therefore the kinetics seem to better fit a first-order and not a second-order rate law.

The kinetics of decomposition of $Cu\text{-}H^+(aq)$ were followed (Figure 2). For pulse intensities yielding 5–40 μM of free radicals this reaction obeyed a first-order rate law with $k = (4.0 \pm 1.5) \times 10^3\ s^{-1}$, independent of $Cu^{2+}(aq)$ concentration in the range (2–10) × 10^{-4} M and pH in the range 3–6. Thus it seems that the major process causing the decomposition of $Cu\text{-}H^+(aq)$ under the experimental conditions is

$$Cu\text{-}H^+(aq) + H_2O \rightarrow Cu^{2+}(aq) + H_2 + OH^-(aq) \tag{14}$$

reactions –1 and 2 being too slow in the concentration range

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(18) The disproportionation of $Cu^+(aq)$ is very slow under the experimental conditions.

studied. (It should be noted that [Cu^{2+}(aq)] cannot be increased due to reaction 9 and the pH lowered due to reaction 7.) When the pulse intensity was increased to yield a total radical concentration of 300 μM, the rate of decomposition of Cu-H^+(aq) increased, probably due to the fact that reaction 3 is an equilibrium process with $K_{-3} \approx 10^3$ s^{-1} and reaction 12 is diffusion controlled. A contribution of reaction 13 under these conditions cannot be ruled out.

The rate of reaction 14 is considerably greater than that of the corresponding reaction for Cl_3CuH^{2-}. For the latter the rate law has the form $d[Cl_3CuH^{2-}]/dt = 5.5 \times 10^2 \times [Cl_3CuH^{2-}][H_3O^+]$, and the intercept of a plot of the rate vs. [H_3O^+] at low acidities has a value of <10 s^{-1}.[8] This result suggests that the rate-determining step in the heterolytic Cu-H^+ bond cleavage involves a nucleophilic attack on the copper atom. The maximum of the spectrum of Cl_3CuH^{2-}[8] seems to be slightly red shifted relative to that of Cu-H^+(aq).

The spectrum of Cu-H^+(aq) is blue shifted relative to those of all other Cu^{II}-R(aq) compounds reported.[4-7] A similar blue shift for $Cr(H_2O)_5H^{2+}$ was attributed to a larger optical electronegativity of hydride than that of most alkyls.[19] The proposal that the mechanism of decomposition of Cu-H^+(aq) is mainly heterolytic is in agreement with that reported for $CuCH_3^+$,[6] $CuCH_2CH_2OH^+$, and $CuCH_2C(CH)_3(H)OH^+$;[4] in none of these is the free radical that should be formed in a homolytic process resonance stabilized.[4] On the other hand, $CuCH_2OH^+$ and $CuCH(CH_3)OH^+$ decompose homolytically.[4] It has been suggested that $Cu^{II}CO_2$ decomposes heterolytically in acid media,[7] the homolytic route being electrostatically unfavorable. However, the reaction $Cu^{II}CO_2 + Cu^{2+} \rightarrow 2Cu^+ + CO_2$ reported in neutral solutions[7] probably involves a homolytic cleavage of $Cu^{II}CO_2$.

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Registry No. Cu^+, 17493-86-6; Cu^{2+}, 15158-11-9; H, 12385-13-6.

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ESCA and UV Photoelectron Spectra of Methyl(trifluoromethyl)germanes, $(CF_3)_{4-n}Ge(CH_3)_n$ (n = 1-3), and Tetrakis(trifluoromethyl)germane, $(CF_3)_4Ge$

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Core-level binding energies have been recorded for germanium 3d and 3p, carbon 1s, and fluorine 1s levels for the series of methyl(trifluoromethyl)germanes, $(CF_3)_{4-n}Ge(CH_3)_n$ (n = 1-3), and for tetrakis(trifluoromethyl)germane, $(CF_3)_4Ge$. The UV-excited photoelectron spectra were also recorded in the range 9-26 eV with use of both He I and He II radiation. Comparisons are drawn to results on related molecules.

Introduction

We have reported the results of our research on the photoelectron spectroscopy of halogen and hydrogen derivatives of (trifluoromethyl)germanes.[2-4] In these studies, the spectra of the (trifluoromethyl)germanium derivatives were compared and contrasted with those of their methyl analogues.[5-7] Therefore, it is appropriate to extend this work to an examination of the mixed methyl-trifluoromethyl series $(CF_3)Ge(CH_3)_3$, $(CF_3)_2Ge(CH_3)_2$, and $(CF_3)_3Ge(CH_3)$, as well as $(CF_3)_4Ge$, in both the X-ray-excited (ESCA) and the UV-excited (He I and He II) regions.

Experimental Section

Core-electron binding energies were determined on a McPherson ESCA-36 photoelectron spectrometer with aluminum Kα X radiation (1486.6 eV) for photoelectron excitation. Samples were introduced in the vapor phase. Argon was bled in to form up to 20% of the total sample and served as an internal standard (argon $3p_{3/2}$ level at 248.68 eV[8]). The general operating details, mode of accumulation, treatment of data, and specific difficulties associated with the recording of spectra of (trifluoromethyl)germanium compounds were as described previously.[2,5] The average full-width at half-maximum of the 1s peaks of C and F were 1.45 and 1.5 eV, respectively. The germanium 3d peaks were broader because of the slight splitting of the $3d_{5/2}$ and $3d_{3/2}$ levels and because the F 2s levels also occur in this region. However, as described in an earlier paper,[2] the Ge 3d orbitals have relatively much larger cross sections than the F 2s so that the average position of the peak can be assumed to be the position of the Ge 3d level. The fact that the trends in the Ge 3p levels parallel those in the 3d lends support to this statement. The half-widths are only slightly larger than those that were observed with use of Mg K X radiation

Table I. Core-Level Binding Energies (eV) for the $(CF_3)_{4-n}Ge(CH_3)_n$ Series

compd	Ge 3d[a]	Ge 3p	C 1s (H)	C 1s (F)	F 1s
$Ge(CH_3)_4$	36.10		289.80		
$(CF_3)Ge(CH_3)_3$	36.90	129.45	290.40	297.20	694.0
$(CF_3)_2Ge(CH_3)_2$	37.55	130.35	291.00	297.70	694.35
$(CF_3)_3Ge(CH_3)$	38.35	131.15	291.45	298.00	694.65
$(CF_3)_4Ge$	39.20			298.60	695.10

[a] Relative to Ne 2s at 48.47 eV.[8]

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