partly from the fact that a specific ligand such as chloride would not be expected to have a constant value as L is changed. The difference between the AOM parameters for the ligands studied to date are outside of the uncertainty limits. In summary, the relative position of triethylphosphine in the two-dimensional spectrochemical series for the $PtCl_3L^{n-}$ series is as follows: for σ donors, $PEt_3 > NMe_3 > C_2H_4 > Cl^- > Br^-$; for π donors, $NMe_3 > Cl^- > PEt_3 > C_2H_4$.

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Registry No. $(Pr_4N)[PtCl_3PEt_3]$, 19508-37-3.

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Kinetics of Formation and Decomposition of the Methyl–Copper(II) Complex in Aqueous Solutions. A Pulse-Radiolysis Study

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The effect of copper ions on the product composition in catalytic free-radical processes in aqueous solutions was interpreted as indicating that short-lived intermediates with copper–carbon bonds are formed in these processes.[1,2] Recently it was shown that indeed reactions 1 and 2 can be followed in aqueous solutions by

$$Cu^{2+}_{aq} + \cdot R \xrightarrow{k_1} [Cu^{III}\text{–}R]^{2+}_{aq} \qquad (1)$$

$$Cu^{+}_{aq} + \cdot R \xrightarrow{k_2} [Cu^{II}\text{–}R]^{+}_{aq} \qquad (2)$$

using the pulse-radiolysis or flash-photolysis techniques[3–6] (where $\cdot R$ is an aliphatic free radical). These techniques enable also the study of the properties of the $[Cu^{III}\text{–}R]^{2+}_{aq}$ and $[Cu^{II}\text{–}R]^{+}_{aq}$ complexes.

In all the systems where reaction 2 was studied, the cuprous ions were prepared in situ by the pulse or flash. The study of reaction 2 was therefore limited to free radicals for which reaction 1 is relatively slow, i.e. $k_1 < 1 \times 10^8$ M^{-1} s^{-1}, and preferably to systems for which the transient $[Cu^{III}\text{–}R]^{2+}_{aq}$ is extremely short lived; i.e., $t_{1/2} < 1$ μs.[3] We wish to report here that one can overcome these limitations by preparing solutions of Cu^{+}_{aq} via

$$Cu^{2+}_{aq} + Cr^{2+}_{aq} \rightarrow Cu^{+}_{aq} + Cr^{III}_{aq} \qquad (3)$$

By use of this reaction, solutions containing $[Cu^{+}_{aq}]/[Cu^{2+}_{aq}] \leq 0.2$ can be easily prepared and kept for several hours.[7] As k_2 is in many systems over two-orders of magnitude larger than k_1, reaction (2) can be directly followed. (The reactions of Cr^{III}_{aq} with aliphatic free radicals are very slow.)[8]

As the methyl radical is the simplest aliphatic free radical and the properties of other free radicals are compared to it, we decided to study the reaction

$$Cu^{+}_{aq} + \cdot CH_3 \rightarrow [Cu^{II}\text{–}CH_3]^{+}_{aq} \qquad (4)$$

The corresponding reaction with Cu^{2+}_{aq} is extremely slow.[5] The properties of $[Cu^{II}\text{–}CH_3]^{+}_{aq}$ were earlier studied applying the flash-photolytic technique.[5] However the limitations of the technique did not enable a detailed kinetic study or product analysis.

Nitrous oxide saturated solutions containing (5–30) × 10^{-4} M $CuSO_4$, (2–20) × 10^{-5} M, Cr^{III}_{aq} and Cu^{+}_{aq}, and 0.1–1.0 M $(CH_3)_2SO$ in the pH range 0.7–5.0 were irradiated by 0.3–1.5 μs pulses of 200-mA 5-MeV electrons. The experimental setup was identical with that described earlier in detail.[3] The pulse intensity was 800–3000 rad. At pH ≥3.0 the following reactions as well as reaction 4[12] have to be considered:

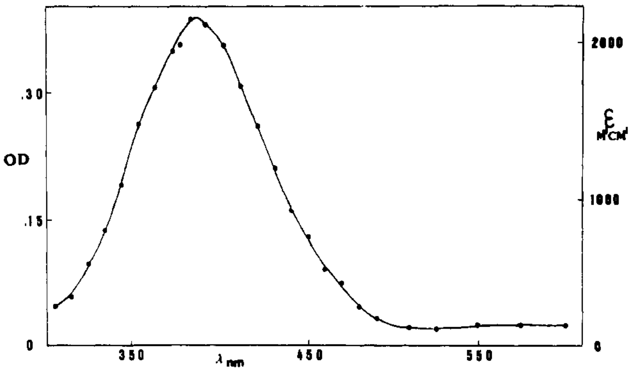

Figure 1. Spectrum of $CuCH_3^{+}{}_{aq}$ measured 10 μs after the pulse: N_2O-saturated solution containing 9 × 10^{-4} M $CuSO_4$, 2 × 10^{-4} M Cr_{aq}^{2+}, and 0.09 M $(CH_3)_2SO$ at pH 3.9; pulse intensity 1500 rad/pulse.

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

$$e_{aq}^- + N_2O \xrightarrow{H_2O} \cdot OH + OH^-_{aq} + N_2 \qquad (6)$$
$$k = 8.7 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$$ [9]

$$e_{aq}^- + Cu^{2+}_{aq} \rightarrow Cu^{+}_{aq} \qquad k = 3.1 \times 10^{10}\ \mathrm{M^{-1}\ s^{-1}} \qquad (7)$$ [9]

$$\cdot H + Cu^{+}_{aq} \rightarrow CuH^{+}_{aq} \qquad (8)$$
$$5 \times 10^9 < k < 2 \times 10^{10}\ \mathrm{M^{-1}\ s^{-1}}$$ [10]

$$CuH^{+}_{aq} \xrightarrow{H_2O} Cu^{2+}_{aq} + H_2 + OH^-_{aq} \qquad (9)$$
$$k = 4 \times 10^3\ \mathrm{s^{-1}}$$ [10]

$$\cdot OH + (CH_3)_2SO \rightarrow \cdot CH_3 + CH_3SOOH \qquad (10)$$
$$k = 7.0 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$$ [11]

In more acidic solutions reaction 11 competes with reactions 6 and 7.

$$e_{aq}^- + H_3O^+ \rightarrow \cdot H \qquad k = 2.0 \times 10^{10}\ \mathrm{M^{-1}\ s^{-1}} \qquad (11)$$ [9]

Under these conditions one might expect a competition between reaction 8 and reaction 12.

$$H\cdot + (CH_3)_2SO \rightarrow (CH_3)_2\dot{S}OH \xrightarrow{H_3O^+} (CH_3)_2S^{\cdot +} + H_2O \qquad (12)$$

The latter reaction has been observed only in strong acidic solutions.[13] We have not detected under our experimental conditions

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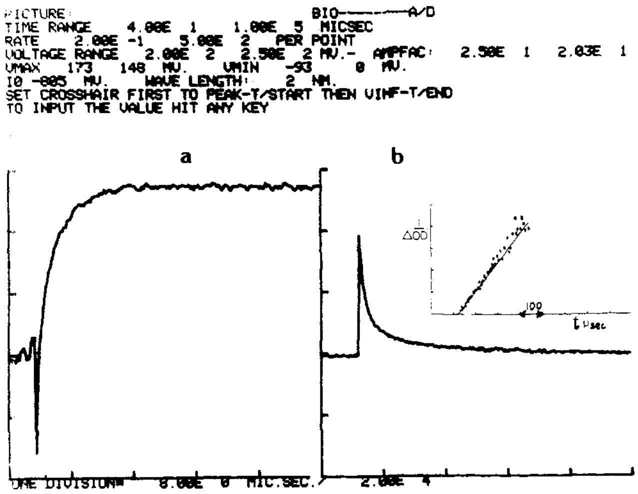

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PICTURE:                                    BIO----------A/D
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RATE    2.00E -1     5.00E  2    PER POINT
VOLTAGE RANGE    2.00E  2   2.50E  2 MV.-   AMPFAC:   2.50E  1   2.03E  1
VMAX   173   148  MV.    VMIN   -93     0  MV.
I0 -805  MV.    WAVE LENGTH:    2  NM.
SET CROSSHAIR FIRST TO PEAK-T/START THEN VINF-T/END
TO INPUT THE VALUE HIT ANY KEY
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Figure 2. Typical kinetic plot for a N_2O-saturated solution containing 9×10^{-4} M $CuSO_4$, 2×10^{-4} M Cr^{2+}_{aq}, and 0.09 M $(CH_3)_2SO$ at pH 3.9. Insert: Fit of the decomposition reaction to a second-order rate law.

in the acidic solutions $0.7 < pH < 3.0$ any transients not observed above pH 3.0; however, the yield of the transient assigned to $CuCH_3{}^+{}_{aq}$, see below, decreased with decreasing pH. These results suggest that either reaction 8 competed efficiently with reaction 12 or that the radical $(CH_3)_2\dot{S}OH$ is unreactive toward $Cu^+{}_{aq}$ and $Cu^{2+}{}_{aq}$ or forms no observable transient when reacting with them.

Thus in solutions at pH $\geqslant$3.0 all the primary free radicals are transformed under the experimentaly conditions into $\cdot CH_3$ radicals during the pulse. Under these conditions one observes the formation of a short-lived transient. The rate of formation of this transient obeys a pseudo-first-order rate law, the rate being proportional to the concentration of $Cu^+{}_{aq}$. We therefore assign the transient to $CuCH_3{}^+{}_{aq}$. The specific rate of reaction 4 calculated from the results is $k_4 = (3.5 \pm 0.4) \times 10^9$ M^{-1} s^{-1} in good agreement with the earlier estimate of Ferraudi of $k_4 \geqslant 10^9$ M^{-1} s^{-1}.[5]

The spectrum of $CuCH_3{}^+{}_{aq}$ (Figure 1) is in good agreement with the partial spectrum reported by Ferraudi.[5] It is of interest to compare the spectra of the Cu^{II}–R complexes reported in the literature. λ_{max} = 340, 375, 395, 395, 450, and 385 nm for CuH^+,[10] $CuCH_3{}^+$, $CuCH_2CH_2OH^+$,[3] $CuCH_2CH(CH_3)OH^+$,[3] $CuCH_2OH^+$,[3] and $CuCO_2$,[6] respectively. These results are in agreement with expectations for a LMCT absorption band. The observed order of λ_{max} is in agreement, where known, with that of the corresponding $(H_2O)Cr^{III}$–R complexes,[14-16] which were also assigned to LMCT transitions. It is of interest to note that the results suggest that the optical electronegativity of unsubsituted alkyl radicals, $\cdot CH_3$, $\cdot CH_2CH_2OH$, and $\cdot CH_2CH(CH_3)OH$, is smaller than that of hydrogen atoms.

The decomposition of $CuCH_3{}^+{}_{aq}$ at pH $\geqslant$2.5 obeys a second-order rate law with $2k = (1.8 \pm 0.2) \times 10^7$ M^{-1} s^{-1}, the rate being independent of the concentrations of $Cu^{2+}{}_{aq}$, $(CH_3)_2SO$, and CH_3CO_2Na; see Figure 2. These results are in disagreement with those of Ferraudi;[5] we have no explanation as to the origin of the discrepancy. In acidic solutions, pH $\leqslant$1.5 the decomposition reaction obeys a first-order rate law; e.g., at pH 1.0 $k_{dec} = (2 \pm 0.5) \times 10^2$ s^{-1}. Aliquots (100-mL) of solutions containing 8×10^{-4} M Cu^{2+}, 2×10^{-4} M Cu^+, 2×10^{-4} M $Cr(III)_{aq}$, and 0.09 M $(CH_3)_2SO$ at pH 3.7 and 1.0 were irradiated by 15 pulses, giving a dose of 5.0×10^4 rad. The gaseous products were analyzed by gas chromatography. In the solutions at pH 3.7, ethane was the product whereas at pH 1.0 methane was the product.

The results thus suggest that at pH $\geqslant$2.5 the decomposition of $CuCH_3{}^+{}_{aq}$ occurs via

$$2CuCH_3{}^+{}_{aq} \rightarrow 2Cu^+{}_{aq} + C_2H_6 \qquad 2k = 1.8 \times 10^7\ M^{-1}\ s^{-1} \tag{13}$$

The mechanism of this reaction does not involve the homolytic decomposition

$$CuCH_3{}^+{}_{aq} \rightleftharpoons Cu^+ + \cdot CH_3 \tag{14}$$

followed by

$$CuCH_3{}^+{}_{aq} + \cdot CH_3 \rightarrow Cu^+{}_{aq} + C_2H_6 \tag{15}$$

or

$$2(\cdot CH_3) \rightarrow C_2H_6 \tag{16}$$

as the observed rate of reaction 13 is independent of the concentration of $Cu^+{}_{aq}$. The results do not enable a detailed analysis of the mechanism of reaction 13, which might occur directly as written or via a rate-determining methyl-transfer reaction

$$2CuCH_3{}^+ \rightarrow Cu(CH_3)_2{}^+{}_{aq} + Cu^+{}_{aq} \tag{17}$$

followed by a fast reductive-elimination step

$$Cu(CH_3)_2{}^+{}_{aq} \rightarrow Cu^+{}_{aq} + C_2H_6 \tag{18}$$

The dependence of the rate of decomposition of $CuCH_3{}^+{}_{aq}$ on the ionic strength, up to 0.1 M $NaClO_4$, was studied. A plot of log k vs. $\mu^{1/2}/(1 + 1.33\mu^{1/2})$ gave a slope of 0.8 ± 0.1, in reasonable agreement with the expected slope of 1.02 for reactions 13 or 17.

The results in acidic solutions indicate that under these conditions the heterolytic decomposition

$$CuCH_3{}^+{}_{aq} + H_3O^+{}_{aq} \rightarrow Cu^{2+}{}_{aq} + CH_4 \tag{19}$$

is faster than reactions 13 or 17.

It is of interest to note that $CuCH_3{}^+{}_{aq}$ decomposes via a bimolecular or a heterolytic process, depending on pH, but not via a homolytic process as observed for $CuCH_2OH^+{}_{aq}$[3] and $[CuCO_2]_{aq}$.[6] This observation indicates that the metal–carbon bond strength in $CuCH_3{}^+{}_{aq}$ is stronger than in $CuCH_2OH^+{}_{aq}$ and $[CuCO_2]_{aq}$. Alternatively this observation might be due to the slow rate of reaction of methyl radicals with $Cu^{2+}{}_{aq}$,[5] which if reaction 15 is also not fast will result in kinetics that apparently do not involve a homolytic contribution.

Registry No. $CuCH_3{}^+$, 67049-30-3; $CH_3\cdot$, 2229-07-4; Cu^+, 17493-86-6.

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Electronic States of Rhodium(I) Binuclear A-Frame Complexes

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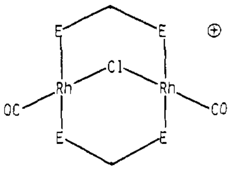
The Rh(I) binuclear A-frame complexes $[Rh_2(CO)_2Cl(dppm)_2]BPh_4$ and $[Rh_2(CO)_2Cl(dam)_2]BPh_4$ with the structure



I

where E = P or As and

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