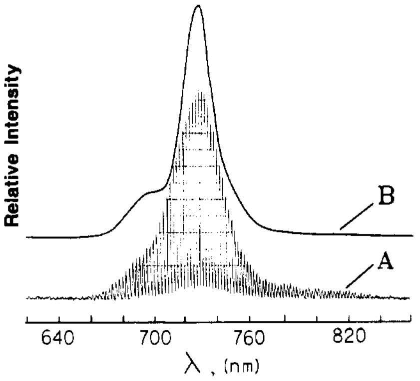

Figure 3. (A) ECL spectrum of a 4 mM $Cr(bpy)_3^{3+}$/MeCN/0.1 M TBAP solution (pulsing limits +2.2 and −1.6 V vs. Ag quasi reference electrode at 0.5 Hz; Pt working and auxiliary electrodes). (B) Photoluminescence spectrum of a 1 mM $Cr(bpy)_3^{3+}$ solution in MeCN on 436-nm excitation.

−2.0 V) with an oxidant generated on stepping the voltage to approximately +2.2 V. ECL were *not* observed when anodic limit potentials of less than +2.0 V were employed—a result in harmony with CV data, which revealed significant background anodic currents only at potentials >+2.0 V. The identity of the oxidant generated at potentials in excess of +2.0 V is as yet unclear, although it is unlikely to be $Cr(CN)_6^{2-}$ due to the general absence of electrochemical evidence for Cr(IV) species in solution.[6] Doubling the supporting electrolyte concentration slightly decreased the ECL intensity, which suggests that TBAP is not the source of the oxidant. Similar results were obtained with $(TBA)BF_4$ as the backing electrolyte. We therefore tentatively assign an adventitious solvent impurity as the origin of the $Cr(CN)_6^{4-}$ oxidant.[21] It is noteworthy that the light pulses were generally observed only upon stepping to the cathodic limit (Figure 2A). This result is consistent with the $Cr(CN)_6^{4-}$ produced in the −2.0 V pulse having a shorter lifetime than the oxidant formed at the anodic limit. The strongest ECL signals were observed in DMF and acetonitrile with a pulse width of 0.5 s, and 1 s for Me_2SO solution.

In view of the rather negative potential for the $Cr(CN)_6^{3-/4-}$ couple and the unusually low energy of the $Cr(CN)_6^{3-}$ ^2E_g excited state (~800 nm emission, 1.5 eV),[20] a range of oxidants might potentially be capable of generating chemiluminescence via reaction with $Cr(CN)_6^{4-}$. We are presently exploring these possibilities further.

B. $Cr(bpy)_3^{3+}$. In keeping with earlier reports,[22] the CV of $Cr(bpy)_3^{3+}$ in acetonitrile exhibited reversible electrochemical behavior on Pt for the $Cr^{3+/2+}$, $Cr^{2+/+}$, and $Cr^{+/0}$ couples. The reduced species $Cr(bpy)_3^{2+}$, $Cr(bpy)_3^{+}$, and $Cr(bpy)_3^{0}$ might all therefore be considered as potential redox precursors to chemiluminescence from the ^2E_g excited state of $Cr(bpy)_3^{3+}$. ac-ECL is in fact observed on pulsing a 4.0×10^{-3} M solution of $Cr(bpy)_3^{3+}$ between +2.2 and −1.6 V, and the ECL spectrum agrees closely with the photoluminescence spectrum of $Cr(bpy)_3^{3+}$ (Figure 3). Electrogeneration of the ^2E_g (O_h) excited state of $Cr(bpy)_3^{3+}$ is thus clearly established.[23]

The intensity of the ECL signal was markedly dependent on the voltage employed as the cathodic limit for the working electrode. At potentials that produce $Cr(bpy)_3^{2+}$ (−0.2 to −0.5 V) and $Cr(bpy)_3^{+}$ (−0.7 to −1.1 V) only very weak signals were observed. A much larger ECL signal was generated on stepping to −1.6 V, where CV data predict formation of $Cr(bpy)_3$. At present we can offer no ready explanation for this interesting intensity dependence on cathodic potential. Finally, the identity of the oxidant in this system has again not been established, although a solvent impurity is considered the most probable source of this species. The ECL signal was maintained for several hours, and only minor deposition on the Pt electrode surface was detected. Once again, emission pulses were observed only as the system was stepped to the cathodic limit, and the strongest signals were detected for a pulse width of 0.5 s.

Acknowledgment. We gratefully acknowledge the Research Corp. and the donors of the Petroleum Research Fund, administered by the Americal Chemical Society, for partial support of this work. The financial support of the Camille and Henry Dreyfus Foundation is also gratefully acknowledged.

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[21] The results obtained on intentional contamination of solutions with small amounts of O_2 and H_2O exclude these species as the oxidant source. In both cases some emission quenching occurred, the effect being especially marked in the case of H_2O. Prior studies have shown that both species also quench $Cr(CN)_6^{3-}$ photoluminescence.[20] A reviewer also suggested the Pt electrode itself may function as the oxidant in these systems. Although an electrode oxidant might result in ECL on stepping to positive potentials, this mechanism will not account for the much greater emission intensity observed on stepping to the cathodic limit potential.

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Contribution from the Nuclear Research Center Negev,
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Kinetics of the Reaction of Copper(I) and Copper(II) Ions with 2,5-Dioxacyclohexyl Free Radicals and Homolysis of the Aqua-Copper(II)-2,5-Dioxacyclohexyl 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.[2,3] Recently it was shown that indeed the reactions

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

$$Cu^{+}(aq) + {}^{\bullet}R \xrightarrow{k_2} [Cu^{II}\text{-}R(aq)]^{+} \qquad (2)$$

can be followed in aqueous solutions by using pulse radiolysis or flash photolysis techniques[4-8] (where $^{\bullet}R$ is an aliphatic free radical). These techniques enable also the study of the properties of the $[Cu^{III}\text{-}R(aq)]^{2+}$ and $[Cu^{II}\text{-}R(aq)]^{+}$ complexes. We have recently shown[8] that one can extend the range of reactions[2] that can be studied 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.[9] As k_2 is in many systems over 2 orders of magnitude larger than k_1, reaction 2 can be directly followed. (The reactions of $Cr^{III}(aq)$

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with aliphatic free radicals are very slow.[10])

With use of these techniques the specific rates of the β-elimination reactions $\mathrm{Cu^{II}{-}CH_2CR^1R^2OH^+(aq) \rightarrow Cu^{2+}(aq) + CH_2{=}CR^1R^2 + OH^-}$ were studied[4-11] and found to be considerably higher than those observed for a series of analogous reactions with different central cations. The higher rates of the β-elimination reactions were tentatively attributed to the tendency of copper(II)–carbon bonds toward homolysis.[12]

We decided to check whether copper(II) also induces cleavage of etheric bonds in analogy to the reactions observed for chromium(III) complexes.[13] A natural choice[14] for such a study is the analysis of the mechanism of decomposition of $\mathrm{Cu^{II}{-}\underline{CHCH_2OCH_2CH_2O}^+(aq)}$ formed via

$$\mathrm{Cu^+(aq) + {}^{\bullet}\underline{CHCH_2OCH_2CH_2O} \rightarrow Cu^{II}{-}\underline{CHCH_2OCH_2CH_2O}^+(aq)} \qquad (4)$$

The results however indicate that the latter complex decomposes homolytically and that the free radicals $\mathrm{{}^{\bullet}\underline{CHCH_2OCH_2CH_2O}}$ thus formed slowly reduce the excess $\mathrm{Cu^{2+}(aq)}$ ions present in the solution.

Nitrous oxide saturated solutions containing (9–90) × 10^{-4} M $\mathrm{CuSO_4}$, (3–30) × 10^{-5} M $\mathrm{Cr^{III}(aq)}$ and $\mathrm{Cu^+(aq)}$, and 0.1–1.0 M $\mathrm{\underline{OCH_2CH_2OCH_2CH_2}}$[15] 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.[4] The pulse intensity was 600–3000 rd. Under these conditions the following reactions have to be considered:

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

$$\mathrm{e^-(aq) + N_2O \xrightarrow{H_2O} {}^{\bullet}OH + OH^-(aq) + N_2} \qquad k = 8.7 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}\ ^{16} \qquad (6)$$

$$\mathrm{e^-(aq) + Cu^{2+}(aq) \rightarrow Cu^+(aq)} \qquad k = 3.1 \times 10^{10}\ \mathrm{M^{-1}\ s^{-1}}\ ^{16} \qquad (7)$$

$$\mathrm{e^-(aq) + H_3O^+ \rightarrow {}^{\bullet}H} \qquad k = 2.0 \times 10^{10}\ \mathrm{M^{-1}\ s^{-1}}\ ^{16} \qquad (8)$$

$$\mathrm{{}^{\bullet}H + Cu^+(aq) \rightarrow CuH^+(aq)} \qquad 5 \times 10^9 < k < 2 \times 10^{10}\ \mathrm{M^{-1}\ s^{-1}}\ ^{17} \qquad (9)$$

$$\mathrm{{}^{\bullet}H/OH + \underline{OCH_2CH_2OCH_2CH_2} \rightarrow H_2/H_2O + {}^{\bullet}\underline{CHCH_2OCH_2CH_2O}} \qquad (10)$$

$$k_{\mathrm{OH}} = 2.0 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}\ ^{17}$$

$$k_{\mathrm{H}} = 1.3 \times 10^7\ \mathrm{M^{-1}\ s^{-1}}\ ^{19}$$

$$\mathrm{{}^{\bullet}\underline{CHCH_2OCH_2CH_2O} + Cu^{2+} \rightarrow Cu^+\ oxidation\ products} \qquad (11)$$

$$\mathrm{2{}^{\bullet}\underline{CHCH_2OCH_2CH_2O} \rightarrow products} \qquad (12)$$

and reaction 4.[20]

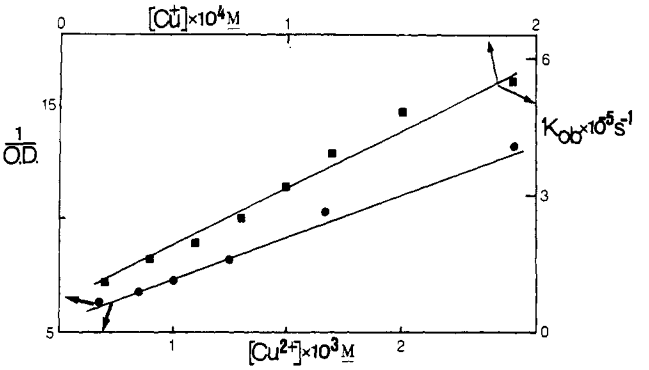

Figure 1. Plot of the observed first-order rate of formation of $\mathrm{Cu^{II}{-}\underline{CH_2OCH_2CH_2O}^+(aq)}$, k_{obsd}, vs. $\mathrm{[Cu^+(aq)]}$ and a plot of 1/OD vs. $1/\mathrm{[Cu^+(aq)]}$ (eq 12).

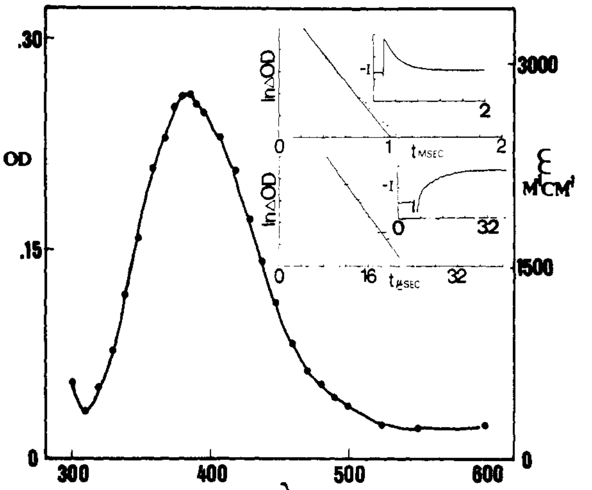

Figure 2. Spectrum of $\mathrm{Cu^{II}{-}\underline{CHCH_2OCH_2CH_2O}^+(aq)}$. Solution composition: 9 × 10^{-4} M $\mathrm{Cu^{2+}(aq)}$, 2 × 10^{-4} M $\mathrm{Cr^{III}(aq)}$, 2 × 10^{-4} M $\mathrm{Cu^+(aq)}$, 0.09 M 1,4-dioxane, pH 2.6, $\mathrm{N_2O}$ saturated. The spectrum was measured 20 μs after a pulse producing 7 × 10^{-6} M of free radicals.

Thus all the primary free radicals are transformed, under the experimental conditions, into $\mathrm{{}^{\bullet}\underline{CHCH_2OCH_2CH_2O}}$ free 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 depending linearly on the concentration of $\mathrm{Cu^+(aq)}$ and being independent of pH, $\mathrm{[Cu^{2+}(aq)]}$, and $\mathrm{[\underline{OCH_2CH_2OCH_2CH_2}]}$ (Figure 1). We attribute therefore the short-lived transient to $\mathrm{Cu^{II}{-}\underline{CHCH_2OCH_2CH_2O}^+(aq)}$ formed in reaction 4. The relatively large intercept in Figure 1, which is independent of pH, $\mathrm{[Cu^{2+}(aq)]}$, and the dose of the pulse, cannot be attributed to reactions 11 and/or 12. The intercept therefore suggests that reaction 4 is an equilibrium process:

$$\mathrm{{}^{\bullet}\underline{CHCH_2OCH_2CH_2O} + Cu^+(aq) \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} Cu^{II}{-}\underline{CHCH_2OCH_2CH_2O}^+(aq)} \qquad (4)$$

From the slope in Figure 1 one obtains $k_4 = (2.5 \pm 0.5) \times 10^9$ $\mathrm{M^{-1}\ s^{-1}}$ and from the intercept $k_{-4} = (8 \pm 2.0) \times 10^4\ \mathrm{s^{-1}}$. From these data $K_4 = (3.1 \pm 1.5) \times 10^4\ \mathrm{M^{-1}}$ is derived.

If $\mathrm{Cu^{II}{-}\underline{CHCH_2OCH_2CH_2O}^+(aq)}$ is indeed formed in the equilibrium reaction 4, then the absorbance[21] due to it, OD, at

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(14) 1,4-Dioxane has the advantage that hydrogen abstraction yields only one type of free radicals, which are all β to an etheric oxygen.

(15) Freshly distilled dioxane was used throughout this study as the presence of traces of peroxides otherwise affected the results.

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(20) The reactions of free radicals, except $\mathrm{e^-(aq)}$ with $\mathrm{Cr^{III}(aq)}$ are known to be very slow[8] and are therefore not considered.

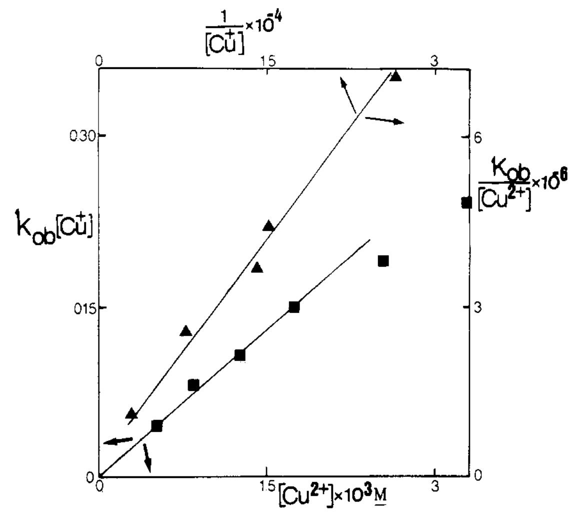

Figure 3. Kinetic relations for the observed rate of decomposition, k_{obsd} of $Cu^{II}-\underline{CHCH_2OCH_2CH_2O}^+(aq)$ according to eq 14. Plots of $k_{obsd}[Cu^+(aq)]$ vs. $[Cu^{2+}(aq)]$ and of $k_{obsd}/[Cu^{2+}(aq)]$ vs. $1/[Cu^+(aq)]$ are shown.

390 nm (where neither $Cu^+(aq)$ nor $^\bullet\underline{CHCH_2OCH_2CH_2O}$ absorb) should obey the equation

$$\frac{1}{OD} = \frac{1}{K_4(OD_\infty)}\,\frac{1}{[Cu^+(aq)]} + \frac{1}{OD_\infty} \qquad (13)$$

where OD_∞ is the absorbance of the transient at saturation, i.e. for $[Cu^+(aq)] = \infty$. A plot of $1/OD$ vs. $1/[Cu^+(aq)]$ (Figure 1) proves this relation. From the intercept one calculates the absorption coefficient of $Cu^{II}-\underline{CHCH_2OCH_2CH_2O}^+(aq)$ at 390 nm $\epsilon(Cu^{II}-\underline{CHCH_2OCH_2CH_2O}^+(aq)) = 3200\ M^{-1}\ cm^{-1}$. From the slope and the intercept $K_4 = (2.0 \pm 0.5) \times 10^4\ M^{-1}$ is derived. This result is in good agreement with that obtained from the kinetic data, and we conclude that $K_4 = (2.5 \pm 1.0) \times 10^4\ M^{-1}$. Thus the free energy gain in reaction 4 is $\Delta G^\circ = -5.7$ kcal/mol.

The absorption spectrum of $Cu^{II}-\underline{CHCH_2OCH_2CH_2O}^+(aq)$ (Figure 2) is similar to that observed for other $Cu^{II}-R^+(aq)$ complexes.[4,7,8,17] We assign therefore the absorption band to a LMCT transition.[8]

When analogous experiments were carried out with $C_2H_5OC_2H_5$ replacing 1,4-dioxane, no analogous transient was observed. This result suggests that "K_4" is significantly smaller for $^\bullet CH(CH_3)OC_2H_5$ radicals than for $^\bullet\underline{CHCH_2OCH_2CH_2O}$ radicals. This is indeed the case for the analogous complexes $(nta)Co^{III}-R(H_2O)^-$ with these free radicals.[11,12]

The kinetics of decomposition of $Cu^{II}-\underline{CHCH_2OCH_2CH_2O}^+(aq)$ obey a pseudo-first-order rate law in $[Cu^{2+}(aq)]$ and an inverse dependence on the concentration of $Cu^+(aq)$, the rate being independent of $[H_3O^+]$ in the pH range 0.5–4.0 and nearly independent of the concentration of 1,4-dioxane. These results indicate that the mechanism of decomposition consists of the equilibrium reaction 4 and reaction 11. For this mechanism the steady-state approximation for the free radical $^\bullet\underline{CHCH_2OCH_2CH_2O}$ yields

$$-d[Cu^{II}-\underline{CHCH_2OCH_2CH_2O}^+(aq)]/dt = \{k_{-4}k_{11}[Cu^{2+}(aq)][Cu^{II}-\underline{CHCH_2OCH_2CH_2O}^+(aq)]\}/\{k_4[Cu^+(aq)] + k_{11}[Cu^{2+}(aq)]\}$$

and as under our experimental conditions $k_4[Cu^+(aq)] \gg k_{11}[Cu^{2+}(aq)]$[23]

$$-d[Cu^{II}-\underline{CHCH_2OCH_2CH_2O}^+(aq)]/dt = (k_{11}/K_4) \times ([Cu^{2+}(aq)]/[Cu^+])[Cu^{II}-\underline{CHCH_2OCH_2CH_2O}^+(aq)] \qquad (14)$$

Therefore plots of $k_{obsd}[Cu^+(aq)]$ vs. $[Cu^{2+}(aq)]$ and of $k_{obsd}/[Cu^{2+}(aq)]$ vs. $1/[Cu^+(aq)]$ should yield straight lines with slopes of k_{11}/K_4 (where k_{obsd} is the experimentally observed first-order rate constant). Such plots are shown in Figure 3; from the slopes one derives $k_{11}/K_4 = 160$ and $140\ s^{-1}$, respectively. Therefore, $k_{11} = (4.0 \pm 0.8) \times 10^6\ M^{-1}\ s^{-1}$.

The results thus indicate that even at pH 0.5 no cleavage of the etheric bond due to β-elimination occurs. If one assumes that the relative rates of the β-elimination reactions for $Cu^{II}-\underline{CHCH_2OCH_2CH_2O}^+(aq)$ and $Cr^{III}-\underline{CHCH_2OCH_2CH_2O}^{2+}(aq)$[13,24] equals the relative rates of the β-elimination reactions for $Cu^{II}-CH_2CH_2OH^+(aq)$[4] and $Cr^{III}-CH_2CH_2OH^{2+}(aq)$,[25] then one calculates for the decomposition of $Cu^{II}-\underline{CHCH_2OCH_2CH_2O}^+(aq)$ via this mechanism at pH 0.5 a specific rate of $3.8 \times 10^2\ s^{-1}$. The observed rate of decomposition under our experimental conditions was always $>1.5 \times 10^3\ s^{-1}$. It is therefore not surprising that we did not observe decomposition via β-elimination.

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(21) Measured immediately after reaction 4 reaches equilibrium and before $Cu^{II}-\underline{CHCH_2OCH_2CH_2O}^+(aq)$ starts to decompose. The two processes are well-separated in time.

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(23) As the highest concentration of $Cu^{2+}(aq)$ used for this calculation (Figure 3) was 2×10^{-3} M and the lowest $Cu^+(aq)$ concentration was 4×10^{-5} M, the error introduced by this assumption is considerably smaller than 8%.

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