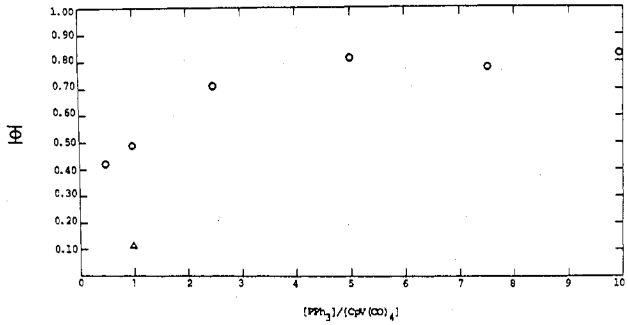

Figure 3. Effect of PPh_3 concentration on the quantum yield (366 nm) of photosubstitution for $CpV(CO)_4$. $[CpV(CO)_4]$ is constant at 0.5×10^{-3} M. Δ = solution saturated with CO.

accuracy of our experimental data, the values obtained are independent of irradiation wavelength. The absence of a wavelength effect on the quantum yield for a photochemical reaction is generally attributed to conversion of the initially populated excited states to a common chemically reactive excited state.[11,16-18]

The variation in quantum yields for substitution of $CpV(CO)_4$ as a function of PPh_3 concentration (Table I and Figure 3) parallels the results obtained for PPh_3 substitution of $CpFe(CO)_2Br$,[19,20] $CpFe(CO)_2I$,[19,20] and 1,1,1,1-tetracarbonyl-2,3,1-diazaferrole.[21] At low phosphine concentrations, the quantum yield increases with increasing ligand concentration. When PPh_3 is present in about fivefold molar excess of $CpV(CO)_4$, the quantum yield reaches a maximum value of 0.80 and becomes independent of entering ligand concentration. An increase in the concentration of free carbon monoxide decreases the quantum yield for phosphine substitution. These results are best accounted for by eq 3–7. Decay

$$CpV(CO)_4 \rightarrow CpV(CO)_4^* \tag{3}$$

$$CpV(CO)_4^* \rightarrow CpV(CO)_4 \tag{4}$$

$$CpV(CO)_4^* \rightarrow CpV(CO)_3 + CO \tag{5}$$

$$CpV(CO)_3 + CO \rightarrow CpV(CO)_4 \tag{6}$$

$$CpV(CO)_3 + PPh_3 \rightarrow CpV(CO)_3(PPh_3) \tag{7}$$

of excited state $CpV(CO)_4^*$ by physical processes is represented by eq 4. Dissociation of carbon monoxide gives coordinatively unsaturated $CpV(CO)_3$ (eq 5), which may be stabilized by weak-bonding interactions with solvent molecules.[21,22] By analogy to other metal–carbonyl systems,[21-24] $CpV(CO)_3$ is expected to recombine rapidly with carbon monoxide, regenerating $CpV(CO)_4$ (eq 6). Thus, PPh_3 must compete with carbon monoxide for the vacant coordination site of the $CpV(CO)_3$ intermediate. As the phosphine concentration is increased, nucleophilic attack by PPh_3 becomes more favorable, and the quantum yield for substitution increases and approaches the quantum yield for formation of $CpV(CO)_3$ (eq 5). The limiting value of 0.80 reveals that loss of carbon monoxide from $CpV(CO)_4^*$ is highly efficient and that it is the dominant photochemical process for $CpV(CO)_4$.

At the suggestion of one of the reviewers we conducted the irradiation of $CpV(CO)_4$ at 366 nm under one atmosphere of ^{13}CO, as we had done for related systems.[19,25] New bands (not observed with ^{12}CO atmosphere) at 2020, 2015, 2000, 1945, 1930, and 1880 cm^{-1} grew in within 3 min. This is attributed to formation of $CpV(CO)_3(^{13}CO)$, *cis*- and *trans*-$CpV(CO)_2(^{13}CO)_2$, and perhaps more heavily ^{13}C enriched species. This result is consistent with the other behavior cited above and is readily explained by eq 5 and 6. Further work is required to definitively assign the infrared bands observed, and this will be undertaken as a separate project.

Although the data could be interpreted in terms of an associative substitution mechanism, it is unlikely that the reaction proceeds by formation of a crowded, eight-coordinate, 20-electron $CpV(CO)_4(PPh_3)$ intermediate. Kinetic studies of the thermal substitution reactions of $CpV(CO)_4$ with a variety of phosphines (including PPh_3) and phosphites have shown that the reactions proceed by a dissociative pathway in which loss of carbon monoxode is the rate determining step.[26] An S_N2 mechanism for nucleophilic substitution has been considered for the photoreaction of $Mn(CO)_4NO$ with PPh_3, but even in this case both dissociative and associative processes are invoked.[27,28]

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Contribution from the Departments of Chemistry,
Indiana-Purdue University at Fort Wayne,
Fort Wayne, Indiana 46805, and
New Mexico State University, Las Cruces, New Mexico 88003

Long-Lived Intermediates in the Production of Hydrogen from Ultraviolet Photolysis of Acidic Di- and Trichlorocuprate(I) Ions[1]

Kenneth L. Stevenson,*[2a] David M. Kaehr,[2b] Dennis D. Davis,[2c] and Charles R. Davis[2d]

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In our previous papers on the photooxidation of di- and trichlorocuprate ions in acid solution we reported on their use as photocatalysts for the oxidation of other species such as Ti^{3+},[3] in the production of $H_2(g)$ via solar energy,[4] and most recently on the primary processes which occur in the photooxidation of these anions.[5] This last report contains strong evidence that the absorption of light into the charge-transfer-to-solvent band of the $CuCl_3^{2-}$ ion results in the production

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(2) (a) Indiana-Purdue University. (b) Graduate research assistant, Indiana-Purdue University. (c) New Mexico State University. (d) Graduate student, New Mexico State University.
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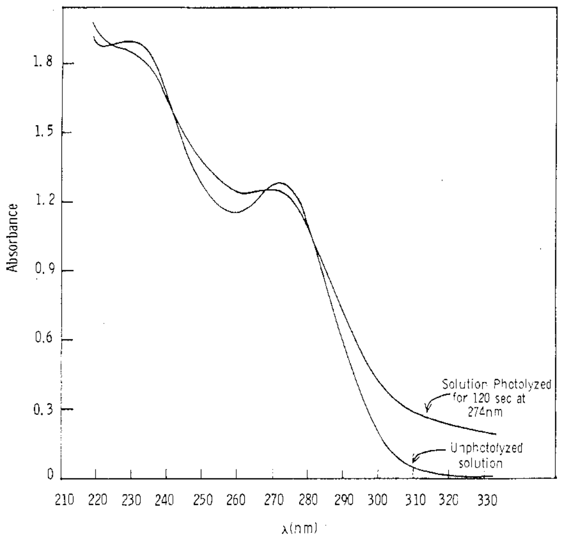

Figure 1. Ultraviolet spectra of unphotolyzed and photolyzed solutions which were initially 0.005 M CuCl in 1 M H^+–0.2 M Cl^-; $\mu = 1$ M, $V = 1.0$ mL, $l = 0.45$ cm, I_0 (at 274 nm) $\simeq 10^{-8}$ einstein s^{-1}, and $t = 1$ min.

of an aquated electron which reduces H^+, as well as the scavengers acetone and N_2O. Ferraudi,[6] who has corroborated this, has proposed that following the initial steps which produce hydrogen atoms, i.e.

$$CuCl_3^{2-} \xrightarrow{274\text{ nm}} CuCl_3^- + e_{hyd}^- \tag{1}$$

$$e_{hyd}^- + H^+ \rightarrow H\cdot \tag{2}$$

either hydrogen atom combination or combination with $CuCl_3^{2-}$ occurs:

$$H\cdot + H\cdot \rightarrow H_2 \tag{3}$$

$$H\cdot + CuCl_3^{2-} \rightarrow HCuCl_3^{2-} \tag{4}$$

The production of $HCuCl_3^{2-}$, which he has postulated to explain his flash photolysis observations, offers a more probable route to H_2 production via

$$HCuCl_3^{2-} + H^+ \rightarrow H_2 + CuCl_3^- \tag{5}$$

During continuous photolysis of a $CuCl_2^-$–$CuCl_3^{2-}$ mixture at $[Cl^-] < 0.4$ and $[H^+] < 1$ M we have observed that hydrogen evolution is preceded by the appearance and disappearance of a yellow species, which has a very long lifetime (i.e., on the order of several hours under optimum conditions) if removed from the light before it disappears. However, the yield of hydrogen is not diminished by the temporary appearance of this species, and thus it must be an intermediate which appears in either the above or an alternate mechanism. We report here our investigations of this yellow species and offer a plausible explanation of its behavior.

Experimental Section

The photolysis system and handling of samples were the same as described previously.[5] However, the photolyses were carried out while the sample cuvette (either a 1- or 0.45-cm thermostated cell) was in the sample compartment of an ACTA M-VI spectrophotometer, allowing for absorbance readings during short interruptions in the photolyses. In addition, several runs were made during which hydrogen evolution was monitored simultaneously with the volumeter attached to the cuvette.[7]

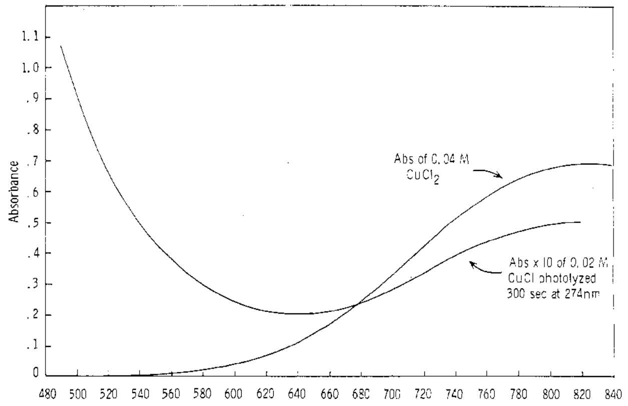

Figure 2. Visible absorption spectra of 0.04 M $CuCl_2$ and 2.0 mL of 0.02 M CuCl photolyzed for 5 min at 274 nm; $I_0 \simeq 10^{-8}$ einstein s^{-1} and $l = 1$ cm. Both solutions contain 1 M H^+–0.4 M Cl^-, at μ = 1 M.

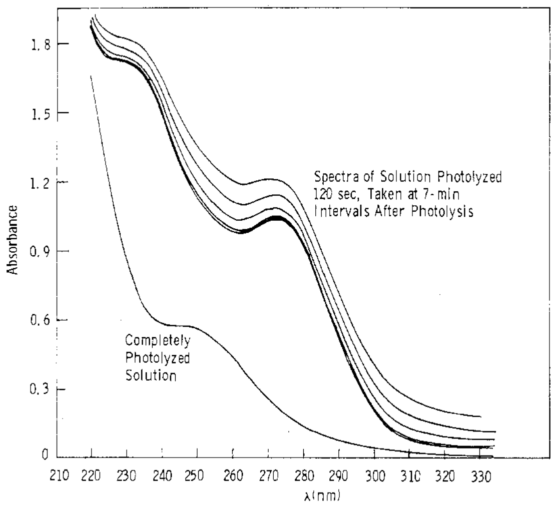

Figure 3. The UV spectral changes during thermal decay of the yellow species taken at 7-min intervals and upon complete photolysis for the same solution as in Figure 1.

The synthesis of the yellow species was achieved nonphotochemically by reacting CuCl solutions containing H^+, Cl^-, Na^+, and ClO_4^- ions at concentrations identical with those used in the photolyzed solutions with $NaBH_4$ such that its concentration was about the same as that of the Cu(I) species in solution.

Results and Discussion

During the photolytic production of the yellow species a series of complex spectral changes, lacking any isosbestic points, occurs in the UV region 220–350 nm. As Figure 1 shows, the UV spectrum of 5×10^{-3} M CuCl in 1 M H^+–0.2 M Cl^- solution before photolysis exhibits two peaks at 274 and 232 nm, which are characteristic of the $CuCl_3^{2-}$ and $CuCl_2^-$ complexes.[5,8,9] After 2 min of irradiation of 1.0 mL of solution in 274-nm light, $I_0 \simeq 10^{-8}$ einstein s^{-1}, the spectrum changes as shown in Figure 1, yielding somewhat flattened peaks and an absorbance at longer UV wavelengths, with a maximum increase at 310 nm. Figure 2 shows the visible spectrum of the same photolyzed solution in the same solvent system. The absorbance at the blue end is unique to the transient whereas the absorbance at 820 nm may well be due to the formation of Cu(II) complexes along with the transient.

To test this hypothesis, the yellow species was allowed to decay in the dark after being formed photolytically. Figure 3 shows the change in the UV spectrum which occurs during the decay. During this decay the absorbance at 820 nm does

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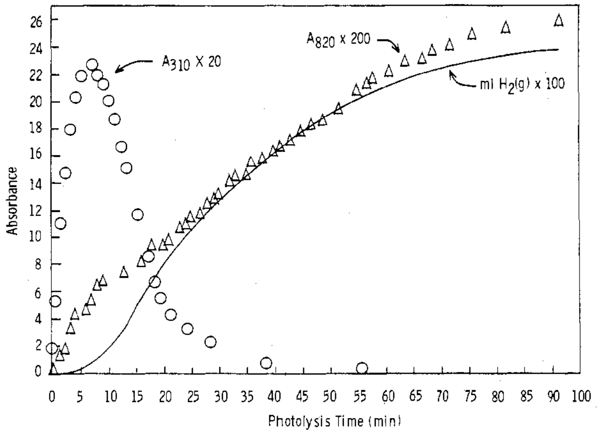

Figure 4. Reaction curves for the photolysis at 274 nm in terms of the absorbances at 310 and 820 nm and the volume of $H_2(g)$ in milliliters for 1.0 mL of 0.020 M CuCl in solution containing 1 M H^+–0.4 M Cl^-; $\mu = 1$ M, $I_0 = 9.7 \times 10^{-9}$ einstein s^{-1}, $T = 301$ K, $P = 740$ torr, and $l = 0.45$ cm.

not change while the blue absorbance disappears (see also Figure 5), indicating that Cu(II) is indeed formed simultaneously with the yellow species and that the 820-nm band is indicative of the amount of Cu(II) formed. In fact, the reduction in copper(I)–chloro complex concentration, as determined by the decrease in absorbance at 274 nm after complete thermal decay of the yellow species, is equal to the amount of Cu(II) species formed as determined by the appearance of the band at 820 nm. Thus it became clear that the course of the reaction could best be followed by monitoring the absorbances at 310 and 820 nm, corresponding to the yellow species and Cu(II) products, respectively.

Figure 4 shows a complete photolysis run in terms of the absorbances at 310 and 820 nm, as well as the volume of H_2 produced. It is apparent that the yellow species and Cu(II) products are produced before any H_2 is evolved and that H_2 evolves only after the onset of decay of the yellow species. Figure 5 illustrates what happens when the photolysis is interrupted at the peak of yellow species concentration. As the yellow species decays thermally between 9 and 70 min on the time scale, there is production of H_2 but no apparent formation of Cu(II) product. Upon resumption of photolysis the yellow species forms again, but to a lesser extent.

The yellow species is easily formed nonphotochemically by adding very small amounts of $NaBH_4$ to the same solutions used in photolysis, giving absorption spectra virtually identical with those of the photochemically produced yellow species. This yellow species, whether formed by photolysis or with $NaBH_4$, is readily adsorbed on an anion-exchange resin (Dowex 1-X8) but not on a cation resin, indicating that it is negatively charged. Unfortunately, it cannot be eluted from the anion resin without being decomposed so that it cannot be obtained in a form which can be easily characterized. Nevertheless, it seems reasonable to suggest that this species may be a hydrido–chlorocuprate(I) complex such as $HCuCl_2^{2-}$ or $HCuCl_3^{3-}$ or some dimeric or polymeric species such as $HCu_2Cl_3^{2-}$ or $HCu_2Cl_4^{3-}$ or a complex mixture of these.

In order for such a copper(I)–hydrido complex to be consistent with the Ferraudi mechanism above, it would have to be formed in a side reaction following step 4. Such a side reaction would involve an electron or H-atom transfer such as

$$HCuCl_2^- + CuCl_2^- \rightleftharpoons HCuCl_2^{2-} + CuCl_2 \qquad (4a)$$

Unfortunately, this system does not yield results as reproducible as one would like in order to make a more detailed analysis of the mechanism and the nature of the yellow species.

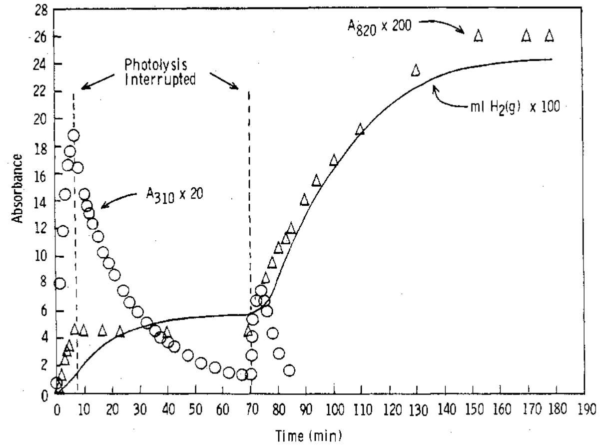

Figure 5. Photolysis and thermal decay curves of same solution as in Figure 4.

For example, the photolysis of identical solutions does not always produce the same maximum amount of yellow species, nor does the yellow species decay at the same rate in the dark. In fact, the decay of the yellow species seems to be sensitive to $[Cu^{2+}]$, to $[H^+]$, and very much to $[Cl^-]$, but it does not appear to decay via any simple rate law. Thus, we are forced to conclude that we may be dealing with a very complex mixture of species rather than a simple monomeric copper(I)–hydrido complex.

Recently, it has been reported that hydride intermediates are observed in the photolytic production of H_2 from acidic solutions of dimeric molybdenum(II)–halo complexes,[10] an anionic system roughly similar to the Cu(I) system we have studied. Indeed, it may well turn out that hydride intermediates are common in many of the H_2-producing reactions involving CTTS photolysis of transition-metal cations or complexes.

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Registry No. $CuCl_2^-$, 15697-16-2; $CuCl_3^{2-}$, 29931-61-1; CuCl, 7758-89-6; $CuCl_2$, 7447-39-4.

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Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214

The Structure of $HGaCl_2$—a Chlorine-Bridged Dimer

O. T. Beachley, Jr.,* and Randall G. Simmons

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The compounds of groups 2A and 3A (primarily Be, Mg, B, and Al) which incorporate both hydrogen and halogen ligands have been the subject of numerous chemical investigations and spectroscopic studies. Interesting structural questions arise for this class of compounds because both hydrogen and halogen atoms can be bridging ligands between metal atoms. The spectroscopic properties of the dimeric group 2A molecules $[HClBeO(C_2H_5)_2]_2$ and $[HClMgO(C_2H_5)_2]_2$ are consistent with structures having bridging hydrogen atoms.[1,2] The hydrogen bridge is also a dominant feature in

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