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Importance of Ground-State Complex Formation in the Cuprous Chloride Sensitized Photoisomerization of *cis,cis*-1,5-Cyclooctadiene to Tricyclo[3.3.0.$0^{2,6}$]octane[1a]

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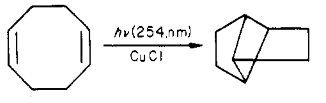
The photoisomerization of *cis,cis*-1,5-cyclooctadiene (ccCOD) to tricyclo[3.3.0.$0^{2,6}$]octane (TCO) in the presence of cuprous chloride has been reinvestigated. Evidence for extensive ground-state complex formation between CuCl and ccCOD in ether solution is presented. Thus 2×10^{-4} mol L^{-1} CuCl is completely complexed at ccCOD concentrations ≥0.02 mol L^{-1}. Under these conditions the complex absorbs the major fraction of the incident radiation at 254 nm. Photolysis at this wavelength leads largely, if not exclusively, to the production of *cis,trans*-1,5-cyclooctadiene (ctCOD). In one or more subsequent photochemical steps, ctCOD is converted to the final photoproduct, TCO. Previous mechanistic schemes for the CuCl-sensitized photoisomerization of ccCOD need to be modified in light of these results.

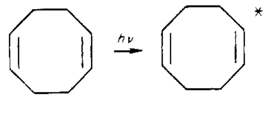
Introduction

Copper(I) compounds sensitize a diverse assortment of olefin photoreactions including rearrangement, cycloaddition, and molecular fragmentation.[2] The first example of such behavior was reported by Srinivasan in a study of the photochemical isomerization of *cis,cis*-1,5-cyclooctadiene (ccCOD) to tricyclo[3.3.0.$0^{2,6}$]octane (TCO) (eq 1) in the presence of cuprous chloride.[3] On the basis of spectral evidence it was argued that, in ether solutions containing CuCl and an appreciable excess of ccCOD, the uncomplexed diene absorbs the major fraction of the incident radiation. Moreover, a reasonable value (<1) for the quantum yield of isomerization could only be calculated on the assumption that free ccCOD was also the major photoactive species in the system. These considerations led to the postulation of a sensitization mechanism (eq 2 and 3) involving the interaction of a photoexcited ccCOD molecule with CuCl. In a subsequent investigation Whitesides et al. examined the photoisomerization of ccCOD in a heterogeneous pentane suspension of the dimeric complex $(CuCl{\cdot}ccCOD)_2$ (1).[4]

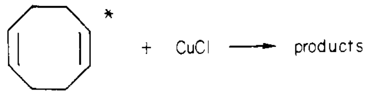


(1)

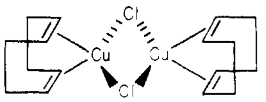
ccCOD TCO



(2)



(3)



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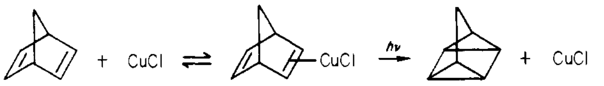
Evidence was presented that the production of TCO does not occur in a single photochemical step but instead involves the intermediacy of *cis,trans*-1,5-cyclooctadiene (ctCOD) and *trans,trans*-1,5-cyclooctadiene (ttCOD). Nonetheless, the primary light-absorbing species present at the outset of the reaction was still assumed to be uncomplexed (i.e., dissociated) ccCOD.

Recent work in this laboratory has demonstrated that cuprous chloride and norbornadiene form an intensely absorbing ground-state complex which, upon being irradiated, generates the highly strained quadricyclene molecule with high quantum efficiency (eq 4).[5] It seemed odd to us that a similar sensitization pathway was apparently absent in the CuCl/ccCOD system since thermodynamic measurements have established that the solution-phase complexes of ccCOD with Cu^+ and Ag^+ are more stable than their norbornadiene analogues.[6] We have therefore reexamined the CuCl-sensitized isomerization of ccCOD, primarily with a view toward identifying the mode of interaction between the two components. Our results are not in accord with earlier studies in that we find evidence for extensive complex formation between CuCl and ccCOD in the ground state. Moreover, we assign this complex, rather than the uncomplexed ccCOD, as the major photoactive species present in solution.



(4)

Experimental Section

Reagents. Anhydrous diethyl ether (Baker) was refluxed with lithium aluminum hydride under nitrogen and was distilled immediately prior to use. Cuprous chloride was prepared by the method of Vogel[7] and was stored in a desiccator. *cis,cis*-1,5-Cyclooctadiene (Aldrich) was distilled on a spinning band column to >99.9% purity (determined by gas chromatography) and was always used within 8 h. *cis,trans*-1,5-Cyclooctadiene was prepared in a pentane solution, in admixture with the cis,cis- and trans,trans isomers, by a method similar to that of Whitesides et al.[4] Tricyclooctane, prepared by the procedure of Srinivasan[8] and Meinwald,[9] was purified to >99.9% by spinning-band distillation and the method of fractional melting.

Spectral and Photochemical Studies. All spectral and photochemical measurements were performed at room temperature (24 ± 2 °C). Electronic absorption spectra were recorded in 1-cm cells on a Cary 15 spectrophotometer. Where a known concentration of CuCl was required, it was weighed out on a microbalance and solubilized in ether by stirring after addition of a sufficient, measured volume of ccCOD (e.g., about 0.5 mg of CuCl, 200 μL of ccCOD, and ether in 25 mL). The CuCl dissolved completely within 1 h at room temperature, and this length of time was therefore also allowed in the preparation of

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[1] (a) Presented in part at the 181st National Meeting of the American Chemical Society, Atlanta, Georgia, March 1981. (b) University of the Witwatersrand. (c) University of Georgia.

[2] Kutal, C.; Grutsch, P. A. *Adv. Chem. Ser.* **1979**, *No. 173*, 325.

[3] Srinivasan, R. *J. Am. Chem. Soc.* **1964**, *86*, 3318.

[4] Whitesides, G. M.; Goe, G. L.; Cope, A. C. *J. Am. Chem. Soc.* **1969**, *91*, 2608.

[5] Schwendiman, D. P.; Kutal, C. *J. Am. Chem. Soc.* **1977**, *99*, 5677.

[6] Hartley, F. R. *Chem. Rev.* **1973**, *73*, 163.

[7] Vogel, A. I. "Practical Organic Chemistry"; Wiley: New York, 1962; p 191.

[8] Srinivasan, R. In "Organic Photochemical Syntheses"; Srinivasan, R., Ed.; Wiley-Interscience: New York, 1971; Vol. 1, p 101.

[9] Meinwald, J.; Kaplan, B. E. *J. Am. Chem. Soc.* **1967**, *89*, 2611.

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ether and ether/ccCOD solutions which were saturated with CuCl. Ether solutions saturated with CuCl were filtered through Whatman's No. 40 paper to avoid any possibility of carry over of suspended solid.

In a typical photochemical run, a 5-mL aliquot of an ether solution containing ccCOD, CuCl, and, where appropriate, nonane[10] was placed in a 1-cm quartz cell fitted with a ground-glass stopper. The solution was purged with nitrogen and then irradiated with a Pen-Ray quartz lamp (Ultra-violet Products).[11] Incident light intensity was measured with ferrioxalate actinometry.[12]

Analyses of ccCOD, TCO, and ctCOD were made by gas chromatography using a 10 ft × $^1/_8$ in. stainless-steel column packed with 5% OV-101 on Chromosorb G HP (80–100 mesh). The operating temperatures of the instrument were as follows: injector, 155 °C; column, 100 °C; detector, 250 °C.[13] Other analytical details were similar to those reported previously.[14]

Results and Discussion

The mechanism of the CuCl-sensitized photoisomerization of ccCOD to TCO (eq 2 and 3) proposed by Srinivasan[3] was based on a number of experimental observations, several of which are not borne out by our experiments. We first summarize these earlier results and then present our own pertinent observations. (1) The solubility of CuCl in diethyl ether was reported to be about 2×10^{-4} mol L^{-1}. (2) ccCOD was found to have an appreciable absorbance at 254 nm. From Figure 1 of ref 3 we calculate an extinction coefficient of ~9.5 L mol^{-1} cm^{-1}. (3) Ether saturated with CuCl absorbed weakly in the ultraviolet, with a maximum optical density of about 0.16 (10-cm cell) at 295 nm. (4) The absorption spectrum of a saturated solution of CuCl in ether to which 3.9×10^{-3} mol L^{-1} ccCOD had been added was nearly the sum of the individual spectra of the components. The presence of a fine suspension thwarted attempts to measure the spectrum of a mixture in which the ether was saturated with CuCl *after* addition of the ccCOD (postsaturation). (5) When solutions of ccCOD in CuCl-saturated ether were irradiated at 254 nm, the quantum yield of TCO production was of the order of 0.1 based upon light absorbed by ccCOD. (6) During photolysis of such solutions, the rate of formation of TCO was approximately proportional to the ccCOD concentration.

In contrast to observation 1, we find that when sufficient CuCl to make a 1.5×10^{-4} mol L^{-1} solution is stirred with ether in a sealed flask for 3 weeks, an appreciable amount of solid CuCl still remains. Moreover, we are unable to reproduce the finding that 2×10^{-4} mol L^{-1} CuCl dissolves in an ether solution containing 3.9×10^{-3} mol L^{-1} ccCOD; in our hands, considerable CuCl is still undissolved after the mixture was stirred overnight.

The ultraviolet absorbance of ccCOD varies considerably between different distilled samples, despite the high purity indicated by gas chromatography. The extinction coefficient measured at 254 nm, for example, has a mean value of 1.0 ± 0.4 L mol^{-1} cm^{-1} for seven samples.[15] Such behavior is suggestive of the presence of trace amounts of strongly absorbing impurities, possibly conjugated olefins or products of air oxidation. The purest sample prepared by us had a 254-nm extinction coefficient of 0.47 L mol^{-1} cm^{-1}. We employ this value, rather than the much higher one quoted in observation 2, in calculating the fraction of incident radiation absorbed by ccCOD.

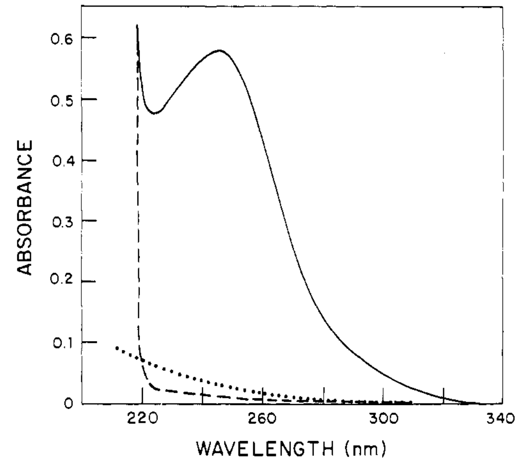

Figure 1. Electronic absorption spectra: (···) ether saturated with CuCl, (- - -) 0.0163 mol L^{-1} ccCOD in ether, and (—) 0.016 mol L^{-1} ccCOD in ether postsaturated with CuCl. Cell path length was 1 cm.

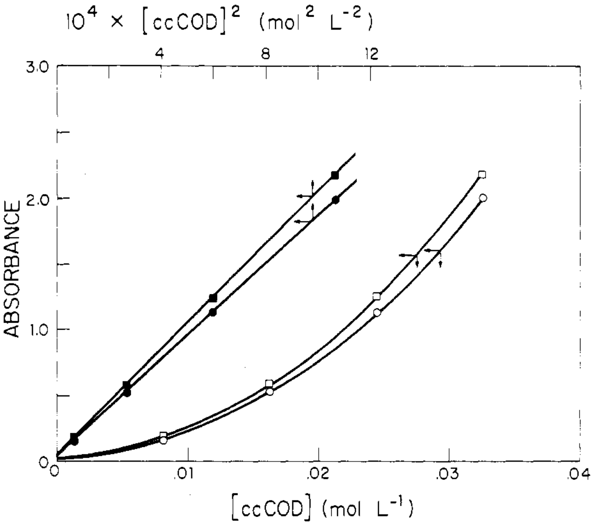

Figure 2. Plots of absorbance vs. [ccCOD] and $[ccCOD]^2$ for ether solutions of ccCOD postsaturated with CuCl: squares and circles correspond, respectively, to absorbances at 246 and 254 nm.

Considerable difficulty was experienced in obtaining high spectral reproducibility below ~250 nm for weakly absorbing ethereal solutions. Our experiments indicate, however, that the absorbance of a saturated solution of CuCl in ether is <0.03 (1-cm cell) at all wavelengths between 240 and 400 nm and is essentially 0.00 above 330 nm. A typical CuCl spectrum is shown in Figure 1.

In agreement with observation 4, the spectra of CuCl-saturated ether and ccCOD in ether are very nearly additive. However, when solid CuCl is stirred with a sufficiently concentrated (≥0.01 mol L^{-1}) ccCOD solution in ether, a substantial increase in absorbance is observed in the 220–320-nm region, with a clear maximum at 246 nm (Figure 1). When

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(10) Nonane was used as an internal standard for gas chromatographic analyses in experiments measuring the quantum yield of TCO formation. Since nonane obscured the ctCOD peak, it was not added when the concentration of the latter was being monitored. In such experiments the long-time concentration of TCO was used as an internal standard based upon its measured quantum yield. Since the detector exhibited nearly identical response factors for TCO and ccCOD, it was assumed that the response for ctCOD would likewise be similar.

(11) The lamp delivers 92% of its output at 254 nm. Quantum yields determined at this wavelength have been corrected accordingly.

(12) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518.

(13) Using a metal column and relatively high temperatures, we could not analyze for the highly reactive ttCOD.[4] Tests showed that some isomerization was occurring in the injection port when a pentane solution of ccCOD, ctCOD, and ttCOD was injected. While this behavior may reflect solely the reactivity of ttCOD, some of it may possibly arise from reactions of ctCOD, which is known to be unstable at 275 °C.[4] In this respect, therefore, our analyses and quantum yield values for ctCOD represent lower limits.

(14) Sterling, R.; Kutal, C. *Inorg. Chem.* **1980**, *19*, 1502.

(15) The absorption spectrum (UV 6093) reported in Vol. 24 of "The Sadtler Standard Spectra—Ultraviolet Spectra" (Sadtler Research Laboratories, Philadelphia) can be used to calculate a 254-nm extinction coefficient of ~1.5 L mol^{-1} cm^{-1} for ccCOD in methanol.

Scheme I[a]

$$\mathrm{CuCl(s)} \underset{}{\overset{K_1}{\rightleftharpoons}} \mathrm{CuCl}$$

$$\mathrm{CuCl + ccCOD} \overset{K_2}{\rightleftharpoons} \mathrm{CuCl{\cdot}ccCOD}$$

$$\mathrm{2CuCl{\cdot}ccCOD} \overset{K_3}{\rightleftharpoons} \mathrm{(CuCl{\cdot}ccCOD)_2}$$

[a] All species exist in solution unless otherwise indicated.

the concentration of ccCOD is varied between 0.02 and 0.1 mol L^{-1}, keeping the nominal concentration of CuCl constant at 1.00×10^{-4} mol L^{-1}, this new absorption feature shows no intensity changes after correction for the absorbance of the ccCOD present. The absorption maximum also follows the Beer–Lambert law up to an absorbance of at least 1.5 when the ccCOD and CuCl concentrations are varied in a fixed ratio. These observations are consistent with the formation of a solution-phase complex or complexes between CuCl and ccCOD, such that essentially all the CuCl in a 10^{-4} mol L^{-1} solution is complexed by 0.02 mol L^{-1} ccCOD. Moreover, when solutions of ccCOD are saturated with CuCl, the resulting corrected absorbance varies linearly with the square of the ccCOD concentration; as seen in Figure 2, plots of absorbance at two different wavelengths vs. $[\mathrm{ccCOD}]^2$ are strictly linear and pass very near to the origin. This square dependence strongly suggests that the *primary light-absorbing species under these conditions is a complex which contains two molecules of ccCOD.*

The spectral behavior that occurs upon mixing CuCl and ccCOD in ether can be understood in terms of the equilibria shown in Scheme I. Designating the individual equilibrium constants as K_1, K_2, and K_3 and the extinction coefficients of the species on the right-hand side of each reaction as ϵ_1, ϵ_2, and ϵ_3, we can express the total absorbance, A (in a 1-cm cell), by eq 5. If the term having a first-order dependence upon

$$A = K_1\epsilon_1 + K_1K_2\epsilon_2[\mathrm{ccCOD}] + K_1^2K_2^2K_3\epsilon_3[\mathrm{ccCOD}]^2 \qquad (5)$$

ccCOD concentration is small, as seems reasonable in view of our observation that conditions of complete complex formation are readily attainable, then eq 5 reduces to eq 6.[16] The latter expression predicts the linear plots of A vs. $[\mathrm{ccCOD}]^2$ observed in Figure 2.[17]

$$A = K_1\epsilon_1 + K_1^2K_2^2K_3\epsilon_3[\mathrm{ccCOD}]^2 \qquad (6)$$

Other schemes of complex formation, involving species such as $(\mathrm{CuCl})_2$ and $\mathrm{CuCl{\cdot}(ccCOD)_2}$, produce the same overall result, the essential requirement being strong absorbance by a species of the form $\mathrm{(CuCl)_{\it x}{\cdot}2ccCOD}$. Evidence supporting the formulation of the absorbing species as $\mathrm{(CuCl{\cdot}ccCOD)_2}$ is the dimeric solid-state structure (1) of the ccCOD complex of empirical formula $\mathrm{C_8H_{12}CuCl}$.[18] If the primary light-absorbing complex in solution does indeed contain two molecules of CuCl, the calculated extinction coefficient at the 246-nm maximum is 1.43×10^4 L $\mathrm{mol^{-1}\ cm^{-1}}$ (1.28×10^4 L $\mathrm{mol^{-1}\ cm^{-1}}$ at 254 nm).

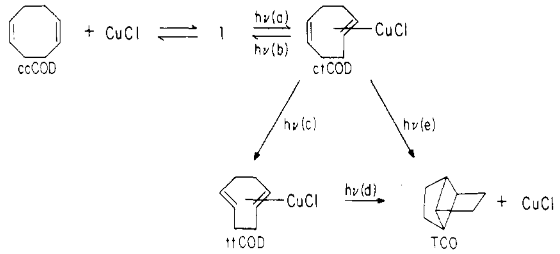
The spectral additivity observed when ccCOD is mixed with an ether solution saturated with CuCl (observation 4) appears, at first glance, to argue against the formation of a ground-state complex. We feel that this interpretation is misleading, however, owing to the very limited solubility of CuCl in ether. Thus even if all the CuCl present in a saturated solution were complexed upon addition of ccCOD, the resulting change in absorbance is expected to be quite small.[19] Considerably more CuCl can be dissolved in ether that already contains ccCOD and, under these conditions, complex formation is clearly evident (Figure 1). Likewise, tetrahydrofuran is an appreciably better solvent for CuCl than is ether; when as little as 0.002 mol L^{-1} ccCOD is added to a saturated solution of CuCl in tetrahydrofuran, a substantial absorbance increase occurs in the ultraviolet region due to complex formation.

Table I. Quantum Yields for TCO Formation (ϕ_{TCO})

[CuCl], mol L^{-1}	[ccCOD], mol L^{-1}	α^a	$\phi_{\mathrm{TCO}}{}^b$
0	0.161	1	<0.004
presaturated	0.0489	>0.4	<0.013
1.29×10^{-4} [c]	0.0408	0.023	0.029 ± 0.005[d]
1.29×10^{-4}	0.0815	0.044	0.033 ± 0.005[d]
1.29×10^{-4}	0.163	0.085	0.037 ± 0.005
1.29×10^{-4}	0.326	0.156	0.033 ± 0.005

[a] Fraction of total exciting radiation that is absorbed by uncomplexed ccCOD. [b] Quantum yields based upon total 254-nm radiation absorbed by the system; error limits are estimated. Solutions were purged with nitrogen for at least 15 min and then irradiated while being stirred. [c] Quantum yields at this CuCl concentration were determined after 1000-s exposures to an incident intensity of 1.84×10^{16} photons s^{-1}. [d] Copper mirror formed during run; ϕ_{TCO} is corrected for this effect but not for decrease of CuCl concentration in solution.

Scheme II



Our efforts to determine quantum yields for the photoproduction of TCO revealed several potential sources of inaccuracy. Air-saturated solutions of CuCl and ccCOD turn yellow-green upon photolysis, indicating oxidation of Cu(I) to Cu(II). In nitrogen-purged solutions, photoreduction of the Cu(I) occurs as evidenced by the deposition of a copper film on the front window of the photolysis cell. This tendency, which can be suppressed by addition of extra ccCOD, lowers the absorbed light intensity due to both the opaqueness of the metallic deposit and the lower concentration of the Cu(I) complex remaining in solution. In ccCOD solutions saturated with CuCl, irradiation produces a solid mixture of CuCl–olefin complexes (the composition of which is discussed below). All of the above complicating factors lead us to assign relatively large error limits to values of the quantum yield for TCO production, ϕ_{TCO} (Table I).

When alone in ether solution, ccCOD is essentially photoinert to 254-nm radiation. In the presence of 1.29×10^{-4} mol L^{-1} CuCl, on the other hand, the diene undergoes conversion to TCO with a greatly enhanced and, apart from a short induction period (vide infra), time-independent quantum yield. Contrary to observation 6, we find no significant increase in the rate of TCO production (as measured by ϕ_{TCO})

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(16) Our data permit us to set a lower limit for the overall formation constant, K, of the complex. From the expression $K = [\mathrm{(CuCl{\cdot}ccCOD)_2}]/[\mathrm{CuCl}]^2[\mathrm{ccCOD}]^2$, and on the conservative assumption that the total CuCl in solution is at least 95% complexed by 0.02 mol L^{-1} of ccCOD, we calculate $K > 5 \times 10^9$ $\mathrm{L^3\ mol^{-3}}$.

(17) Although the A-axis intercepts of these plots could be interpreted as $K_1\epsilon_1$, the absorbance of a saturated solution of CuCl, we feel that these deviations from the origin are just as likely due to small systematic errors.

(18) van den Hende, J. H.; Baird, W. C. *J. Am. Chem. Soc.* **1963**, *85*, 1009.

(19) The solubility of CuCl can be estimated from spectral data. Assuming that the small absorbance change (≤0.04 in a 1-cm cell) that occurs upon mixing excess ccCOD with CuCl-saturated ether arises from the conversion of the dissolved CuCl to complex 1, we calculate a solubility of $\sim 6 \times 10^{-6}$ mol L^{-1}. Although admittedly approximate, this value is considerably smaller than that reported previously[3] and is more in line with our observations concerning the limited solubility of CuCl.

Scheme III

Class 1: Photoexcitation of a Preformed Copper–Olefin Complex

$$\mathrm{Cu(I)} + \text{olefin} \rightleftharpoons \mathrm{Cu(I)}\text{–olefin} \xrightarrow{h\nu} [\mathrm{Cu(I)}\text{–olefin}]^* \rightarrow \mathrm{Cu(I)} + \text{product}$$

Class 2: Bimolecular Interaction between an Excited State of the Olefin and the Ground-State Cu(I) Compound

$$\text{olefin} \xrightarrow{h\nu} \text{olefin}^* \xrightarrow{\mathrm{Cu(I)}} [\mathrm{Cu(I)} + \text{olefin}^*] \rightarrow \mathrm{Cu(I)} + \text{product}$$

Class 3: Bimolecular Interaction between an Excited State of the Cu(I) Compound and Ground-State Olefin

$$\mathrm{Cu(I)} \xrightarrow{h\nu} \mathrm{Cu(I)}^* \xrightarrow{\text{olefin}} [\mathrm{Cu(I)}^* + \text{olefin}] \rightarrow \mathrm{Cu(I)} + \text{product}$$

when the concentration of ccCOD is increased from 0.0408 to 0.326 mol L^{-1} at a fixed CuCl concentration (Table I). Since the percentage of the incident radiation absorbed by the uncomplexed diene increases sixfold under these conditions, this result argues strongly against the assignment of ccCOD as the major photoactive species in solution (eq 2 and 3). The fraction of light absorbed by $(CuCl{\cdot}ccCOD)_2$, on the other hand, experiences only a modest decrease (~16%). The relative insensitivity of ϕ_{TCO} to total diene concentration can thus be accounted for by *assigning this ground-state complex as the principal photoactive species initially present in solution.*

In attempting to explain why many of our results are at odds with earlier findings, we can point to the need for exceptional purity of the ether and ccCOD and for rigorous exclusion of air during photolysis. Although Srinivasan reportedly obtained TCO by irradiating ccCOD in ether which had been saturated with CuCl (observation 5), it is possible that some inadvertent carry over of solid CuCl, perhaps as a suspension, could have led to those results. We find the quantum yield of TCO production to be negligible (Table I) in solutions that have been saturated with CuCl and then carefully filtered prior to addition of ccCOD.

One further point which was investigated relates to the possible involvement of ctCOD and ttCOD as intermediates in the reaction. Whitesides et al.[4] showed that both of these isomers were present in complexed, solid form, during the photolysis of complex 1 suspended in pentane. They further established that irradiation of free ttCOD in solution produced TCO in high yield, while ctCOD produced TCO and ccCOD only upon irradiation in the presence of excess CuCl.

We have also observed that the photolysis of ether or tetrahydrofuran solutions of ccCOD saturated with CuCl produces a precipitate consisting of a mixture of CuCl–olefin complexes. Treatment of this mixture with aqueous sodium cyanide liberates the olefins which were identified as ctCOD (largest component), ccCOD, and ttCOD (smallest component) by gas chromatography.[20] At the same time, in solution, the amount of ctCOD is barely detectable, while no ttCOD is found. These results suggest that the cis,trans and trans,trans isomers are produced photochemically and form stronger, less soluble complexes with CuCl than does the cis,cis isomer.[4] During irradiations of nitrogen-purged ether solutions of ccCOD and a sufficiently low CuCl concentration to avert formation of any precipitated complex, it is possible to monitor the time dependence of the ctCOD and TCO concentrations in solution.[21] As shown in Figure 3, there is a definite induction period preceding the appearance of TCO (none is detectable after 50 s), during which time the concentration of ctCOD rises rapidly. We infer from this behavior that ctCOD is a primary photoproduct while TCO is formed at a significant rate only in one or more secondary processes. Since the initial slope of the curve for ctCOD formation is about six times that of the TCO curve at the steady state (where $\phi_{TCO} \simeq 0.033$; Table I), the quantum yield of ctCOD production must be ~0.2. It is important to note that this value exceeds the fraction of the total exciting radiation absorbed by uncomplexed ccCOD (0.09). Such behavior, which seems incompatible with the mechanism suggested by Srinivasan (eq 2 and 3),[22] lends additional support to our assignment of $(CuCl{\cdot}ccCOD)_2$ (the only other absorbing species) as the principal photoactive species initially present in solution.

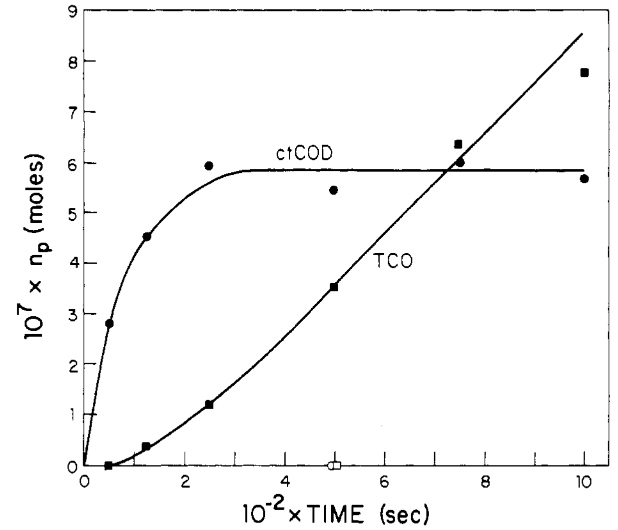

Figure 3. Time development of the amount of product (n_p) formed during irradiation of an ether solution containing 1.44×10^{-4} mol L^{-1} CuCl and 0.161 mol L^{-1} ccCOD: (●) ctCOD, (■) TCO. Open circle and square denote amounts of ctCOD and TCO, respectively, formed upon irradiating 0.161 mol L^{-1} ccCOD in the absence of CuCl.

On the basis of our spectral and photochemical results, we propose that the CuCl-sensitized conversion of ccCOD to TCO in ether solution involves most or all of the steps contained in Scheme II. An essential feature of this mechanism is the formation of a ground-state cuprous chloride–ccCOD complex (a likely structure for which is 1). Irradiation into the intense ultraviolet absorption band of this complex leads initially to the production of ctCOD which, in one or more subsequent steps, is converted to TCO. Detailed knowledge of these latter processes, particularly the involvement of ttCOD as an intermediate, remains scanty. Thus our data are inadequate to assess the relative importance of the direct (step e) and indirect (steps c and d) routes from ctCOD to TCO or, in the indirect route, whether free or complexed ttCOD is the main precursor of TCO.

The applicability of the mechanism in Scheme II to the photochemical behavior of pentane suspensions of the dimeric complex 1 remains to be considered. The chief difference between this mechanism and the earlier version proposed by

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(20) Special conditions (e.g., glass column, low temperatures) similar to those employed by Whitesides et al.[4] are required to detect ttCOD.

(21) Our analysis for ctCOD did not establish the relative proportions of the free and uncomplexed forms of the diene present in solution.

(22) Srinivasan's mechanism would predict that the observed quantum yield can be no higher than the percentage of the total irradiation that is absorbed by uncomplexed ccCOD. This assumes, as seems reasonable, that at least one photon must be absorbed by the diene per product molecule formed.

Whitesides et al.[4] resides in the identity of the primary light-absorbing species present at the onset of irradiation. In an attempt to clarify this point, we performed the following experiment. The suspension that forms upon stirring 70 mg of **1** with 10 mL of pentane[23] was filtered, and the absorption spectrum of the resulting solution was measured. The absorbance in the ultraviolet region was found to (i) possess a maximum at ~246 nm (cf. Figure 1) and (ii) be considerably larger than that expected if CuCl and uncomplexed ccCOD were the only absorbing species present.[24] These observations provide convincing evidence for the presence of a ground-state cuprous chloride–ccCOD complex in solution. Moreover, this complex, rather than free ccCOD, accounts for the major fraction of the total radiation absorbed by the system. It seems likely, therefore, that the mechanism in Scheme II also governs the photochemical behavior of pentane suspensions of **1**.

Concluding Remarks

In a recent survey of the Cu(I)-sensitized photoreactions of olefins, we categorized the mechanisms by which these processes occur into three general classes.[2] These are presented in Scheme III, where the symbol Cu(I) is used in a generic sense to denote some Cu(I) compound. Of the photoreactions surveyed, the CuCl/ccCOD system provided the lone example of a class 2 mechanism. This assignment must now be seriously doubted in view of the compelling evidence that a ground-state complex plays a pivotal role (i.e., class 1 behavior) in the sensitization process. Indeed, we feel that a class 2 mechanism constitutes, at most, a minor pathway in this system.

In a broader context, it is worthwhile to consider the conditions under which a class 2 mechanism might be expected to occur. Inasmuch as this pathway involves the interaction of a photoexcited olefin with a ground-state Cu(I) species, the lifetime of the olefin excited state must be sufficiently long to permit this bimolecular process to compete effectively with other modes of deactivation. Under the assumption that (1) bimolecular sensitization occurs with a diffusion-controlled rate constant of 10^{10} L mol^{-1} s^{-1} (a typical value for diffusion in common organic solvents)[25] and (2) the concentration of Cu(I) is 2×10^{-4} mol L^{-1}, it can be shown that the lifetime of the olefin excited state must be $>1 \times 10^{-7}$ s in order to attain a sensitization quantum yield of 0.2. Generally, the lowest lying singlet and triplet states of olefins which are not constrained to rigid geometries possess lifetimes appreciably shorter than this value since rapid radiationless deactivation may occur via a twisting motion about a C=C bond.[26,27] Since the 1,5-cyclooctadiene framework is reasonably flexible as evidenced by the isolation of three isomeric forms, the unimportance of a class 2 sensitization mechanism in this system is not surprising. The obvious, though unproven corollary of the above argument is that olefins which cannot undergo facile twisting motions should be more prone to this type of mechanism because of longer excited state lifetimes.

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Registry No. ccCOD, 1552-12-1; CuCl, 7758-89-6; TCO, 250-21-5.

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[23] These quantities correspond to those used in ref 4.

[24] For example, the absorbance at the 246-nm maximum is 0.24, whereas a value <0.05 should be observed if CuCl and ccCOD were the only absorbing species in solution.

[25] Calvert, J. G.; Pitts, J. N. "Photochemistry"; Wiley: New York, 1966; p 627.

[26] Turro, N. J. "Modern Molecular Photochemistry"; Benjamin/Cummings: Menlo Park, CA, 1978; Chapter 5.

[27] Kropp, P. J. In "Organic Photochemistry"; Padwa, A., Ed.; Marcel Dekker: New York, 1979; Vol. 4, Chapter 1.

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Properties of New Aquo Ions Obtained on Reduction of the Trinuclear Aquomolybdenum(IV) Ion $Mo_3O_4^{4+}$ †

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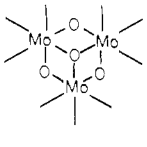
Reduction of the Mo(IV) aquo ion, $Mo_3O_4^{4+}$, with Zn/Hg or by electrochemical methods at a potential ca. −0.25 V (vs. NHE) in *p*-toluenesulfonic acid (HPTS) and $[H^+] = 0.5$–4.0 M gives a new green aquo ion which titrates for Mo(III). The ion is oxidized by ClO_4^- as well as O_2 and is characterized by a spectrum (λ_{max}, nm (ϵ, M^{-1} cm^{-1} per Mo)) with adsorptions at 420 (sh) (ca. 100), 635 (80), and 825 (45). The ease of chemical and electrochemical reoxidation to Mo^{IV}_3 suggests that the essential trinuclear core structure is retained. The Mo^{III}_3 ion is more strongly held on a cation-exchange column than the 4+ Mo^{IV}_3 ion, consistent with protonation of bridging oxo ligands. Cyclic voltammetry studies suggest minor structural changes prior to formation of Mo^{III}_3. On addition of Mo^{III}_3 to Mo^{IV}_3, electrochemical reduction of Mo^{IV}_3, or (partial) oxidation of Mo^{III}_3, preferably at $[H^+] \geq 4.0$ M, a mixed-oxidation-state species is obtained which titrates for $Mo^{III}_2Mo^{IV}$ and has absorption maxima at 398 (230), 495 (sh) (ca. 115), and 1050 (100). At lower $[H^+]$, the extent of formation decreases, and at $[H^+] \leq 0.5$ M it is <30%. Consistent with these observations, when the $[H^+]$ (<4.0 M) of solutions of $Mo^{III}_2Mo^{IV}$ is decreased, amounts of Mo^{III}_3 and Mo^{IV}_3 are obtained. Reduction potentials determined in 2 M HPTS are −0.10 V for $Mo^{IV}_3 + 2e^- \rightleftharpoons Mo^{III}_2Mo^{IV}$ and −0.18 V from experiments involving oxidation of the Mo^{III}_3 species, $Mo^{III}_2Mo^{IV} + e^- \rightleftharpoons Mo^{III}_3$. No evidence was obtained for a $Mo^{III}Mo^{IV}_2$ ion.

Introduction

It has now been established that the Mo(IV) aquo ion is a triangulo trinuclear species having an $Mo_3O_4^{4+}$ core structure, with three water molecules coordinated to each molybdenum.[1]



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† No reprints available.