Catalytic Role of Copper(I) in the Photoassisted Valence Isomerization of Norbornadiene

Dwight P. Schwendiman and Charles Kutal*

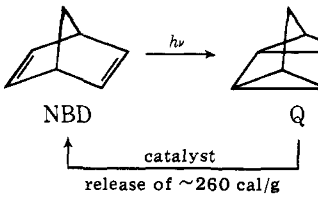
Contribution from the Department of Chemistry, University of Georgia, Athens, Georgia 30602. *Received February 10, 1977*

Abstract: A detailed investigation of the photoassisted valence isomerization of norbornadiene (NBD) to quadricyclene (Q) in the presence of copper(I) salts is reported. In the prototypal cuprous chloride-norbornadiene system, spectral evidence indicates that a 1:1 ClCu-NBD π complex is present in solution and is, in fact, the photoactive species. Quantum yield data obtained in several solvents and at different initial NBD concentrations support this premise. The photoreaction is thought to originate via population of an olefin-metal charge-transfer state of the complex. Possible pathways by which this excited state yields Q are considered. The absence of NBD photodimerization products suggests that Cu(I) salts containing strongly binding anions have little tendency to coordinate more than one NBD molecule.

Numerous reactions of organic molecules are accelerated by light in the presence of catalytic amounts of transition-metal compounds. Recently studied examples of such metal-catalyzed, photoassisted processes include hydrogenation,[1] polymerization,[2] double bond migration,[3] fragmentation,[4] and cis-trans isomerization.[5] A general mechanistic scheme for photoassistance is depicted in eq 1.[6] The metal, M, is thought to modify the reactivity of the organic substrate, S, via formation of a M-S complex (step 1), which subsequently undergoes conversion to product, P (step 2), followed by the release of P in the system (step 3). Light may assist in one, two, or all three of the steps shown.[7]

$$\mathrm{M} + \mathrm{S} \overset{\text{step 1}}{\rightleftharpoons} \mathrm{M\text{-}S} \overset{\text{step 2}}{\rightleftharpoons} \mathrm{M\text{-}P} \overset{\text{step 3}}{\rightleftharpoons} \mathrm{M} + \mathrm{P} \qquad (1)$$

As part of our investigation[8] of the reversible valence isomerization of norbornadiene (NBD) to quadricyclene (Q) as an attractive process for the chemical storage of solar energy (eq 2), we have examined the effect of various transition metal compounds on the photoassisted forward reaction. In particular we recently reported[9] that this transformation proceeds efficiently in the presence of catalytic amounts of cuprous chloride. The direct involvement of a cuprous chloride-norbornadiene π complex was proposed. The apparent specificity of the pathway leading from this complex to Q is somewhat surprising in view of the proclivity of transition-metal compounds to catalyze thermal and photochemical cycloadditions of NBD.[10-12]



(2)

To better understand the nature of the Cu(I)-NBD interaction in solution and its mechanistic role in favoring the photoassisted production of Q, we have undertaken a series of detailed spectral and photochemical studies. We report here the effects of solvent, NBD concentration, and coordination environment about Cu(I) on the quantum efficiency of the photoreaction. In addition the apparent lack of copper-catalyzed photodimerization of NBD has been assessed in detail.

Experimental Section

(a) Reagents. Norbornadiene (Aldrich) was refluxed with potassium metal under nitrogen, and freshly distilled prior to each spectral and photochemical run. The distillate was kept under nitrogen to minimize the formation of peroxides. An unidentified impurity is observed in the gas chromatogram of freshly distilled NBD; the size of this peak remains unchanged, however, during subsequent photolysis. Authentic samples of quadricyclene were prepared by the method of Smith.[13]

All solvents were at least reagent grade quality. Ethanol and chloroform were dried and purified by standard techniques.[14] Acetonitrile, ether, and tetrahydrofuran (THF) were dried over molecular sieves and deaerated prior to use.

Cuprous chloride and cuprous bromide were prepared by literature methods[15] and stored under nitrogen in a desiccator. Cuprous iodide (Fisher) was purified by Soxhlet extraction using acetonitrile as solvent. The complex ClCu-NBD was prepared as a pale cream-yellow solid by the method of Haight et al.[16] Anionic $CuCl_2^-$ was formed in ethanol solution by addition of excess anhydrous LiCl to a suspension of CuCl. Cuprous acetate[17] was synthesized by reacting $CuCO_3$ with glacial acetic acid in acetic anhydride. The resultant blue-green solid was dried at 110 °C under vacuum and was reduced with Cu metal strips in an acetonitrile-acetic acid-acetic anhydride solvent mixture. An extremely air-sensitive pale yellow solid is obtained upon isolation and washing with ether.[18] The CuOAc-NBD complex was generated in situ in neat NBD.[19] $Cu(hfa)_2$ (hfa is the anion of 1,1,1,5,5,5-hexafluoro-2,4-pentanedione) was prepared by a literature method.[20]

The exo-trans-exo dimer of norbornadiene was synthesized by the procedure of Arnold et al.[21] The white crystalline solid possessed the correct elemental analysis and melting point (Anal. Calcd: C, 91.23; H, 8.76. Found: C, 91.15; H, 8.94; mp 63-66 °C (lit. 67-78 °C). The infrared and NMR spectra were also supportive of the dimer structure. The high boiling dimer was eluted at 150-190 °C (depending upon the particular column) using temperature programed gas chromatography. Typically, the temperature was raised from 60 or 80 to 240 °C at a rate of 20 °C per min.

(b) Spectral Studies. Electronic absorption spectra were measured on a Cary 15 spectrophotometer. Absorbance by uncoordinated NBD was subtracted from the sample spectrum by including an equal concentration of the diene in the reference cell. Infrared spectra were obtained on a Perkin-Elmer 621 spectrometer, while NMR spectra were run on a Varian HA-100 spectrometer.

(c) Photochemical Studies. All solutions were prepared under a nitrogen atmosphere, since the introduction of moisture or air into a sample resulted in the oxidation of Cu(I). The occurrence of this process was readily detected by a distinct yellow to yellow-green coloring of the solution; however, the resultant Cu(II) species proved to be photoinactive (vide infra).

In a typical run the copper(I) compound was weighed out on a Cahn electrobalance and then stirred with freshly distilled NBD and solvent. The resulting solution was centrifuged, and a 3-mL aliquot was pipetted into a 1-cm rectangular quartz cell equipped with a side arm to facilitate purging with nitrogen prior to photolysis. Irradiations were performed using a water-cooled, 450-W medium-pressure mercury arc lamp mounted in a merry-go-round apparatus similar to one described in the literature.[22] The 313-nm mercury line was isolated with a half-width of 23 nm by means of suitable blocking filters. Light intensity was determined by ferrioxalate actinometry.[23]

The intensity, I_a, of the light absorbed by the photoactive species

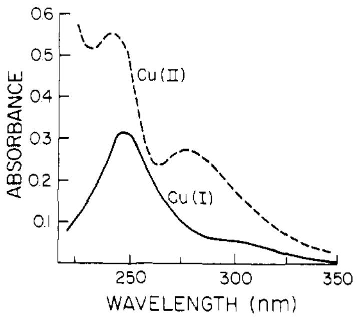


Figure 1. Electronic absorption spectra of Cu(I) and Cu(II) salts in the presence of 0.1 M NBD in ethanol: (—) 6.0×10^{-4} M CuCl, (- - -) 9.6×10^{-4} M $Cu(NO_3)_2{\cdot}3H_2O$ + 1.2×10^{-3} M LiCl.

is calculated using eq 3:

$$I_a = \frac{\epsilon_a c_a}{\sum_i \epsilon_i c_i}[1 - e^{-2.303(\Sigma_i \epsilon_i c_i)l}]RI_0 \qquad (3)$$

which is presented in general form to account for possible inner filter effects. The symbols have the following meanings; ϵ and c are the extinction coefficient and concentration, respectively, of an absorbing species in solution, the subscript a refers to the photoactive species, the summation is taken over all i absorbing species (including a), l is the cell path length, R is a scaling factor, and I_0 is the incident light intensity. In the limiting case where a is the sole absorbing species, both summation terms reduce to $\epsilon_a c_a$. The factor R compares the percent of incident light absorbed by the sample to that absorbed by the actinometer. Typically a solution containing 5×10^{-3} M CuCl and 1 M NBD (in a 1-cm cell) has an absorbance around 2.5 at 313 nm, but only about 0.9 at the long-wavelength cutoff at 325 nm. By comparison the absorbance at the short-wavelength cutoff at 302 nm is approximately 4.0. The value of R was therefore calculated as follows. The percent of incident light absorbed by the sample or the actinometer could be calculated from their spectra using Beer's law. These values were then plotted as a function of wavelength and the resultant curves integrated by the cut and weigh method. Typically $R > 0.9$ for 5×10^{-3}M CuCl-1.0 M NBD solutions; at the smallest CuCl concentrations employed, $R \simeq 0.5$.

The irradiated samples were analyzed for NBD and Q by gas chromatography using a Varian 2700 gas chromatograph equipped with a flame ionization detector and a 6 ft × ⅛ in. 1.5% OV-101 on Chromosorb W (80-100 mesh) column. The operating temperatures of the instrument were: injector, 135-140 °C; column, 75-80 °C; detector, 250 °C. Flow rates of nitrogen carrier gas were between 20 and 30 mL/min. The number of moles of Q formed was determined by comparing the gas chromatographic peak areas (measured by planimetry) of irradiated samples to those of nonirradiated standards. In ethanol or chloroform solutions, the solvent peak provided a convenient internal standard. The ratio of the NBD and Q peak areas is a direct measure of the isomeric composition as the detector response is essentially identical for equal concentrations of the two compounds. With the small percentage conversions routinely obtained in the photochemical runs, however, it is difficult to completely separate the Q signal from the residual tailing of the solvent peak. For this reason the quantum yields listed in Table II may be underestimated by 10-20%.

Results and Discussion

(a) Electronic Spectra. A 1.0 M solution of freshly distilled NBD in ethanol or chloroform is spectrally transparent above 295 nm. Because of limited solubility, we were unable to obtain an accurate spectrum of CuCl in these solvents, although its spectrum has been reported in ether.[24] Solutions of CuCl ($1-5 \times 10^{-3}$M) and a 100-fold excess of NBD exhibit an intense absorption band in ethanol (λ_{max} 248 nm, $\epsilon = 6.3 \times 10^3$ M^{-1} cm^{-1}; Figure 1), chloroform (λ_{max} 253 nm, $\epsilon = 7.9 \times 10^3$ M^{-1} cm^{-1}), or THF (λ_{max} 255 nm, $\epsilon = 5.7 \times 10^3$ M^{-1} cm^{-1}). This band, which is absent in the spectra of the parent compounds, has previously been assigned[9a] as a metal-olefin charge-transfer transition characteristic of a cuprous chloride-norbornadiene π complex. A shoulder at 300 nm is discernible in ethanol ($\epsilon = 8.3 \times 10^2$ M^{-1} cm^{-1}) and THF ($\epsilon = 8.8 \times 10^2$ M^{-1} cm^{-1}) but is partially obscured by the higher band in chloroform ($\epsilon = 8.5 \times 10^2$ M^{-1} cm^{-1}).

Table I. Spectral Data for the CuCl-Norbornadiene System in Ethanol

[CuCl], M × 10^4	[NBD], M	$A_{300\ nm}$[a]
4.25	0.100	0.325
4.32	0.100	0.302
4.27	0.100	0.348
4.32	0.145	0.373
4.27	0.145	0.355
4.32	0.199	0.357
4.27	0.199	0.336
4.25	0.297	0.327
4.27	0.297	0.380
4.25	0.347	0.343
4.25	0.396	0.368
4.32	0.496	0.325
4.27	0.496	0.396
4.27	0.496	0.388
4.25	0.496	0.369
4.25	0.692	0.352
4.27	0.889	0.355
4.25	1.28	0.384
4.32	1.28	0.390
4.27	1.28	0.425
		0.358 ± 0.019[b]

[a] Absorbance at 300 nm in a 1-cm cell. [b] A similar constancy of the absorbance with changes in [NBD] is observed at other wavelengths; thus $A_{280\ nm} = 0.624 \pm 0.013$.

A detailed spectral study of the cuprous chloride-norbornadiene system in ethanol solution is summarized in Table I. The data were treated by the method originally developed by Benesi and Hildebrand.[25] Thus, a plot of [CuCl]/A (A is absorbance at a fixed wavelength) vs. 1/[NBD] yields an essentially horizontal straight line,[26] the result of A remaining constant with increasing NBD concentration in the range 0.1-1.28 M. While such behavior has previously been interpreted[9a] in terms of the formation of a single absorbing cuprous chloride-norbornadiene complex in solution, there is precedent to suggest that a more complicated situation may obtain. Thus, it has been reported[27] that Cu(I) complexes containing one, two, three, and even four coordinated olefinic bonds possess sufficiently similar electronic absorption spectra that a spectral distinction between them becomes impossible. Consequently, it would appear that spectral results in Table I can be rationalized equally well by the formation of either a single complex or varying proportions of two (or more) stoichiometrically distinct, but spectrally indistinguishable complexes. Further discussion of this question will be deferred until after consideration of the photochemical results.

CuCl is readily soluble and stable in acetonitrile. Addition of 0.1 M NBD to an acetonitrile solution containing 1×10^{-3} M CuCl only slightly shifts the spectrum to longer wavelengths. The increase in absorbance at 300 nm is <8% of that expected for complete complexation of the cuprous salt (assuming an $\epsilon_{300\ nm}$ value comparable to that in ethanol). Similarly, the absorbance of a 1×10^{-3} M CuCl-0.1 M NBD solution in 1:1 ethanol-acetonitrile is only 37% of the same solution in pure ethanol. These results clearly indicate that acetonitrile hinders complex formation. Addition of NBD to a solution of CuCl in ether resulted in the precipitation of a pale yellow solid. Insufficient complex remained dissolved to enable reliable measurement of the spectrum.

No discernible interaction occurs between NBD and simple Cu(II) salts. Thus, addition of 0.1 M NBD to a 5.87×10^{-4} M $CuCl_2{\cdot}2H_2O$ solution in ethanol causes no change in the absorption spectrum. Similarly, the spectrum of a 1:1 solution

Table II. Quantum Yields at 313 nm for the Photoassisted Isomerization of NBD to Q in the Presence of Cu(I)

Data set	[NBD], M	Cu(I) compd	Solvent	Quantum yield 5 h	10 h	24 h	ϕ_{av}[a]	
A	9.86 (neat)	CuCl				0.39 ± 0.07	0.39 ± 0.07	(5 values)
B	1.0	CuCl	Ethanol	0.23 ± 0.04	0.24 ± 0.01	0.33 ± 0.04	0.28 ± 0.05	(16 values)
C	0.10	CuCl	Ethanol	0.40 ± 0.04	0.29	0.36 ± 0.07	0.36 ± 0.06	(5 values)
D	1.0	CuCl	Chloroform	0.33 ± 0.02	0.37 ± 0.02	0.37 ± 0.03	0.35 ± 0.02	(11 values)
E	0.10	CuCl	Chloroform	0.27			0.27	(1 value)
F	0.50	CuCl	THF				0.42	(1 value)
G	0.50	CuCl	Acetonitrile				*b*	
H	9.86	CuOAc					0.42	(1 value)
I	0.50	CuCl + LiCl[c]	Ethanol				0.36	(1 value)
J	0.50	CuCl + LiCl[d]	Ethanol				0.29	(1 value)

[a] Average of all values in a particular data set; where quoted, error limits represent mean deviation. [b] No detectable Q production. [c] [LiCl]/[CuCl] = 5.5. [d] [LiCl]/[CuCl] = 22.9.

of $Cu(NO_3)_2 \cdot 3H_2O$ and LiCl ([Cu(II)] = 10^{-3} M) is unaffected by the addition of 0.1 M NBD; furthermore, a clear spectral distinction exists between NBD solutions containing Cu(II) and those containing Cu(I) (Figure 1).

(b) **Photochemical Data.** In preliminary experiments the photoassisted conversion of NBD to Q was found to occur with comparable rates in the presence of either CuCl or CuBr.[28] In contrast, solutions of CuCl irradiated under similar conditions were only about 10% as effective. This result may be due to incomplete light absorption by the sparingly soluble cuprous iodide-norbornadiene complex. Of the copper(I) halides, CuCl was chosen for detailed study because it could be obtained in highest purity and generally presented the fewest handling problems. Qualitatively, the same degree of Q production occurs whether CuCl or an authentic sample of ClCu-NBD is added to the NBD containing solutions. The solid ClCu-NBD complex, however, is extremely air and moisture sensitive and is relatively more difficult to preserve pure than is CuCl. Therefore in all the photochemical studies the complex was formed in situ by addition of CuCl to excess NBD in solution.

The quantum yields of Q production at 313 nm in the presence of CuCl are listed in Table II as a function of solvent, initial NBD concentration, and time of irradiation. Similar values are obtained in neat NBD, ethanol, chloroform, and THF, suggesting that solvent assumes no major role in the photoreaction. At the reagent concentrations employed in these solvents, >99% of the CuCl is complexed by NBD. In contrast, the strong solvation of Cu(I) by acetonitrile[29] hinders complex formation (vide supra), thus accounting for the lack of photoreactivity in this solvent.

The quantum yield remains sensibly constant as a function of initial NBD concentration over a 100-fold range (data sets A-E). This fact is particularly evident when comparing ϕ_{av}, the average of all the quantum yield values obtained under a specific set of conditions (but at various irradiation times). Likewise, no trend in quantum yield with time of irradiation (at a given initial NBD concentration) is evident.

At the [NBD]/[CuCl] ratios (typically ≥100) employed in this study, the most probable photoactive species in solution are the 1:1 (eq 4) and 1:2 (eq 5) cuprous chloride-norbornadiene complexes:[30]

$$\mathrm{CuCl + NBD \overset{K_{11}}{\rightleftharpoons} ClCu\text{-}NBD} \tag{4}$$

$$\mathrm{ClCu\text{-}NBD + NBD \overset{K_{12}}{\rightleftharpoons} ClCu\text{-}(NBD)_2} \tag{5}$$

Accordingly, three distinct situations may arise: (i) ClCu-NBD is present exclusively, (ii) ClCu-$(NBD)_2$ is present exclusively, or (iii) both complexes are present in significant amounts, but are spectrally indistinguishable (vide supra). We tend to discount alternative ii on grounds that it would require an unreasonably large value ($\gtrsim 10^2$)[26] of K_{12}. Thus, 1:2 complex formation has been reported to be negligible in 2-propanol solutions containing 10^{-3} M Cu^+ and 0.01-1 M NBD,[31] conditions which are comparable to those employed in the present study. If alternative iii were to obtain, the relative proportions of ClCu-NBD and ClCu-$(NBD)_2$ should vary as a function of NBD concentration. The absence of a discernible concentration dependence of the quantum yield, however, demands that both the 1:1 and 1:2 complexes are photoactive and, furthermore, that they possess essentially identical quantum yields for Q production. While such behavior cannot be totally discounted, it would be fortuitous indeed. For this reason we feel that the combined spectral and photochemical data (also see section f) are more simply accommodated in terms of the 1:1 ClCu-NBD complex being the only significant photoactive species in solution. Further discussion will therefore be directed along this line.

Changing the anion from Cl^- to OAc^- has little effect on the quantum yield (Table II). This result may reflect the fact that CuOAc also forms a 1:1 complex with NBD (thought to be $[CuOAc\text{-}NBD]_2$) in solution.[19]

No Q is detected when solutions of $Cu(NO_3)_2 \cdot 3H_2O$ in ethanol or $Cu(hfa)_2$ in methylene chloride, each containing 0.5 M NBD, were irradiated for 10 h. The latter result is interesting in view of the recent report of the interaction of $Cu(hfa)_2$ with olefins in solution.[32]

We have found no evidence for thermal or photochemical interaction of CuCl with Q in deaerated solutions.[33] Thus, irradiation of CuCl and 0.5 M Q in ethanol for 16 h produces no detectable NBD. Upon exposing the sample to air, however, Cu(I) is oxidized and Q is destroyed with no concurrent production of NBD. In an experiment designed to examine this process, two separate samples containing 2.92×10^{-3} M CuCl and 0.5 M NBD in ethanol were irradiated for 15 h. One sample was analyzed immediately and then again after sitting for 24 h. The second sample was analyzed only after the 24-h period. In the first case, the amount of Q initially detected in the irradiated solution decreased 20.4% during the 24 h following air exposure and sampling, and the solution became dark green in color. In the air-tight sample tested after 24 h, the Q concentration was within 3% of that initially measured in the first sample. The rate of Q decomposition under the conditions described above is $\sim 6.3 \times 10^{-4}$ M/h. The decomposition products were not identified.

(c) **Catalytic Nature of the Reaction.** The photoassisted valence isomerization of NBD to Q is catalytic in CuCl. Typical catalytic factors (moles of Q produced/mol of CuCl present) are listed in Table III. Continued irradiation would undoubtedly have increased these values, which thus represent lower limits in the systems studied.

(d) **Effect of Cu(I) Coordination Environment on the Quantum**

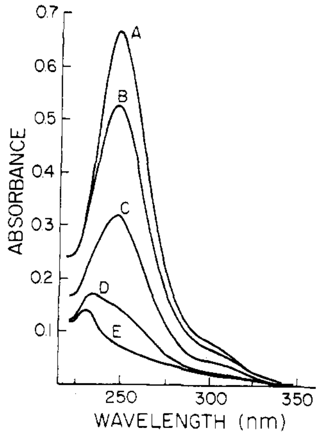


Figure 2. Spectral changes upon addition of LiCl to an ethanol solution containing 1 × 10^{-3} M CuCl and 0.1 M NBD. LiCl/CuCl ratio: (A) 0; (B) 0.48; (C) 1.03; (D) 2.63; (E) 15.3.

Yield. In an attempt to increase the effective Cu(I) concentration in solution, we "solubilized" CuCl in ethanol by adding an excess of Cl^-. The predominant species formed is $CuCl_2^-$,[34] which exhibits a band at 229 nm ($\epsilon = 1.52 \times 10^3$ M^{-1} cm^{-1}) in its electronic absorption spectrum. This band rapidly tails off at longer wavelengths and is considerably less intense than the absorption due to the ClCu-NBD complex. Neither the band maximum nor intensity change as a function of the Cl/CuCl mole ratio over a range of 1:1 to 30:1, and no new peaks are observed in the spectrum.

When NBD and excess Cl^- are added to a solution containing CuCl, they compete for coordination sites on the metal (eq 6):

$$\mathrm{ClCu\text{-}NBD} + \mathrm{Cl}^- \overset{K_3}{\rightleftharpoons} \mathrm{CuCl_2}^- + \mathrm{NBD} \qquad (6)$$

As shown in Figure 2, stepwise addition of Cl^- to an ethanol solution containing 1.0 × 10^{-3} M CuCl and 0.1 M NBD results in the disappearance of the spectrum characteristic of ClCu-NBD and the concomitant formation of the 229-nm band indicative of $CuCl_2^-$. Assuming that eq 6 identifies the major species in solution, we can calculate the concentration of $CuCl_2^-$ from eq 7:

$$[\mathrm{CuCl_2}^-] = \frac{A/l - (\epsilon_{\mathrm{ClCu\text{-}NBD}})C_0}{(\epsilon_{\mathrm{CuCl_2}^-}) - (\epsilon_{\mathrm{ClCu\text{-}NBD}})} \qquad (7)$$

where A is the absorbance, l is the cell path length, C_0 is the initial concentration of CuCl, and $\epsilon_{\mathrm{ClCu\text{-}NBD}}$ and $\epsilon_{\mathrm{CuCl_2}^-}$ are the indicated extinction coefficients at a particular wavelength. The percent $CuCl_2^-$ present in solution is listed in Table IV as a function of the Cl^-/CuCl mole ratio. Even at a 1:1 mole ratio, >50% of the CuCl is complexed as $CuCl_2^-$.

Also listed in Table IV are values of $\epsilon_{\mathrm{CuCl_2}^-}{}^{229\ \mathrm{nm}}$, calculated from eq 7 using the experimental absorbance readings, the previously calculated concentrations of $CuCl_2^-$, and a value of $\epsilon_{\mathrm{ClCu\text{-}NBD}}{}^{229\ \mathrm{nm}} = 2.89 \times 10^3$ M^{-1} cm^{-1}. Although there is considerable scatter in the values calculated at different Cl^-/CuCl ratios, the generally good agreement with the experimentally measured quantity (1.52 × 10^3 M^{-1} cm^{-1}) suggests that the equilibrium described by eq 6 is the predominant process occurring in the solution studied. Further support for this premise emerges from the data in Table II. Thus, if ClCu-NBD is the sole photoactive species in solution, the quantum efficiency for Q production (calculated using eq 3) should remain invariant upon addition of Cl^-. A comparison of the quantum yield values obtained in the presence (data sets I and J) and absence (data sets B and C) of added Cl^- reveals that, within typical experimental uncertainty, this situation does obtain.

Table III. Catalytic Activity of CuCl

[CuCl], M	$[NBD]_0$, M[a]	$[Q]_f$, M[b]	% conversion	Catalytic factor[c]
2.03 × 10^{-3}	0.50	0.431	86.2	212
5.10 × 10^{-3}	1.00	0.450	47.8	88
5.12 × 10^{-3}	3.00	0.459	15.8	90
6.91 × 10^{-3}	9.86 (neat)	0.869	9.1	126
6.43 × 10^{-3}	9.86	2.53	25.7	394

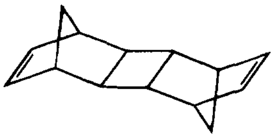
[a] Initial concentration of NBD present. [b] Final concentration of Q formed. [c] Moles of Q formed/moles of CuCl present.

Table IV. Competition of Cl^- and NBD for CuCl in 0.1 M NBD-Ethanol Solution

LiCl/ CuCl	% $CuCl_2^-$ [a]	$\epsilon_{\mathrm{CuCl_2}}{}^{229\ \mathrm{nm}} \times 10^{-3}$, M^{-1} cm^{-1}
0.48	25.1	1.05
0.83	40.2	1.76
1.17	60.0	1.49
2.63	77.7	1.57
4.60	82.3	1.75
5.75	89.6	1.53
14.1	94.6	1.38
		1.50 ± 0.17

[a] Percentage of total Cu(I) in system present as $CuCl_2^-$; calculated from eq 7 using appropriate spectral data at 248 nm.

(e) **Assessment of Dimerization as an Alternative Pathway.** The possible occurrence of Cu(I)-catalyzed, photoassisted dimerization of NBD was investigated in detail. While several different NBD dimers have been reported depending upon the reaction conditions, the exo-trans-exo structure (I) appears to be among the most commonly encountered.[10] The analogous dimer is the predominant product obtained upon irradiating solutions of the structurally similar monoolefin, norbornene, and Cu(I) salts.[9b,27,35]



I

The presence of I was sought in the following experiment. An ethanol solution containing 4.81 × 10^{-3} M CuCl and 1.0 M NBD was irradiated 24 h, giving a quantum yield for Q production of 0.28. The total area after irradiation was low by 8.3% (vide infra), which is equivalent to the disappearance of 0.083 M NBD or the formation of 0.042 M I if dimerization has occurred. This concentration, if present, is easily detectable via gas chromatography. However, no major new peaks are observed up to a final temperature of 240 °C.

Increasing the amount of NBD should enhance the cycloaddition reaction, due to the likely second-order dependence of the rate of this process on NBD concentration. Accordingly, a 6.9 × 10^{-3} M CuCl solution in neat NBD was irradiated for 7.5 days. Analysis by gas chromatography revealed two product peaks: Q (9.03% relative area) and I (0.036% relative area). The latter was identified by running an authentic sample of the dimer under identical conditions. The dimer concentration is thus only 0.4% of that of Q.

One additional photoproduct was observed with retention time approximately equal to that of Q. Since its area was typically only 1.5% of the Q area, however, we did not investigate this minor species further.

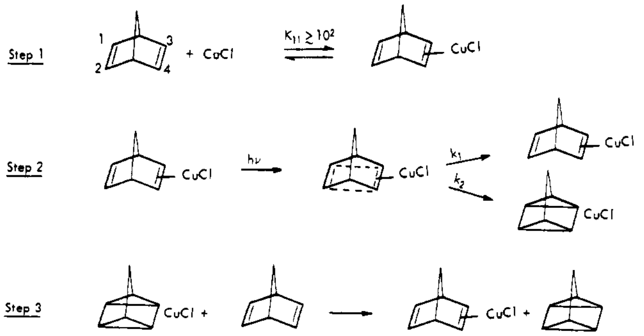
While photoassisted dimerization does not appear to be a major competing pathway in the systems examined, two additional observations suggest the presence of another process (besides the minor one noted in the preceding paragraph). (1) Initially clear solutions of CuCl and NBD (0.1 or 1 M) in chloroform or (especially) ethanol form a fine, white particulate suspension in over 50% of the photochemical runs. A similar suspension appears (though less frequently) in nonirradiated samples. (2) The integrated gas chromatographic peak area of the irradiated sample does not necessarily equal the area of the nonirradiated standard.

Most often the area of the irradiated sample had decreased relative to that of the standard, although occasionally the area was larger (ranging from +0.6 to +8.1%). The percent decrease in area ranged from −0.02 to −27.6% (one instance) with an average decrease of −7.15%. The decrease in total area does not statistically worsen as the time of irradiation increases or as the NBD concentration changes. For example, the total area of a sample of 3.4×10^{-3} M CuCl in 0.5 M NBD-ethanol solution is low by −7.77% at 5 h, −5.24% at 10 h, and −10.37% at 24 h. By comparison, a similar solution irradiated 72 h shows no decrease (<0.05%) in total area.

The sporadic nature of the decreases in the total NBD + Q peak area and the fact they do not appreciably worsen upon prolonged photolysis suggest that such behavior is not due to an inherent photoreaction of the ClCu-NBD π complex, but is instead attributable to the presence of adventitious impurities. Although all reagents were carefully purified and dried, and all solutions were handled under a nitrogen atmosphere, it is difficult to completely exclude oxygen and moisture during sample preparation. Any traces of these contaminants could initiate facile radical processes resulting in the disappearance of NBD and/or Q. Thus in the absence of an appropriate radical inhibitor, NBD has been reported to self-polymerize to an insoluble white powder within a few hours at room temperature.[36] If similar $(NBD)_n$ ($n > 3$) species are formed in the systems investigated in the present study,[37] low volatility would undoubtedly preclude their detection by gas chromatography. Depending upon whether the irradiated or nonirradiated (standard) solutions experience a greater amount of polymerization, the total NBD + Q peak area would appear to decrease or increase, respectively, following photolysis. We are currently investigating this problem in more detail, with the aim of finding a suitable (nonabsorbing, nonreactive toward Cu(I)) radical inhibitor.

(f) Mechanistic Considerations. The photoassisted valence isomerization of NBD to Q in the presence of Cu(I) salts conforms to the general mechanism outlined in eq 1. Each of the pertinent steps is depicted in more detail in Scheme I for the thoroughly studied CuCl + NBD system.

Scheme I



Step 1. Rapid formation of a ClCu-NBD π complex ensues upon mixing the parent compounds in solution. The solid-state structure of the complex exists as tetrameric $(ClCu\text{-}NBD)_4$ units in which each copper atom is bonded in an exo configuration to one NBD molecule.[38] While we earlier presented evidence that the 1:1 stoichiometry persists in solutions containing a large excess of NBD, smaller units (dimers, trimers) consistent with this empirical formula could conceivably be present. Thus, the complex will be represented generically as ClCu-NBD in the ensuing discussion, with no implication as to its true molecular formula.

Step 2. The ClCu-NBD π complex is characterized by an intense metal-olefin charge-transfer band which effectively increases the absorption of the system out to ~350 nm (Figure 1). Irradiation of this band with 313-nm light may, depending upon the direction of electron flow, populate the lowest unoccupied (charge transfer to olefin) or depopulate the highest occupied (charge transfer to metal) π molecular orbital on norbornadiene.[39] In either instance the net result of this electron redistribution is a weakening of the bonding between C_1-C_2 and C_3-C_4 with a concurrent enhancement of that between C_1-C_3 and C_2-C_4.[40] Subsequent relaxation (vide infra) of the excited state occurs by pathways leading to NBD (k_1) and Q (k_2).

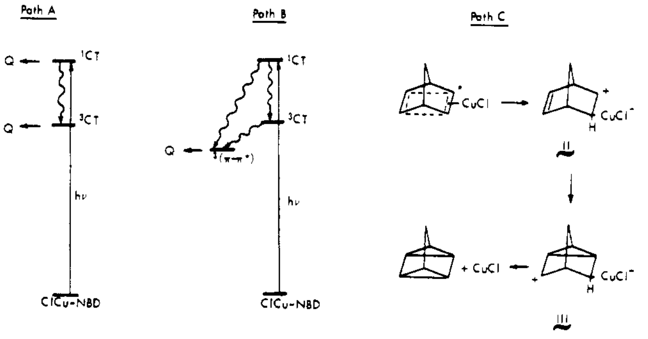
Step 3. The newly formed Q molecule, having little affinity for CuCl, is readily displaced from the immediate coordination sphere of the metal by NBD. The ClCu-NBD complex is thus regenerated, accounting for the catalytic role of the metal in the photoassisted process. As long as sufficient NBD is present in solution to ensure complete complexation of CuCl, the quantum yield should remain independent (Table II) of the NBD concentration.

A mechanism similar to that presented in Scheme I is likely to obtain in the cases of CuBr and CuOAc, since both salts undergo complex formation with NBD. Indeed this mechanism may prove to be fairly general for Cu(I) compounds capable of forming stable NBD complexes. As discussed previously, the strongly bound NBD molecule can undergo a significant perturbation upon photoexcitation of the complex, thus generating a potentially reactive species.

The generally accepted Chatt-Dewar description[41] of the bonding in metal-olefin complexes identifies two major components: (1) σ donation from a filled olefin π orbital to an empty metal orbital, and (2) π-back donation from a filled metal d orbital to an empty π^*-olefin orbital. Both components appear to contribute to the stability of the Cu(I)-NBD bond.[30c] In contrast, Cu(II) salts exhibit little tendency for backbonding and interact only weakly with olefins,[32] thus accounting for their inability to catalyze the NBD to Q photoisomerization.

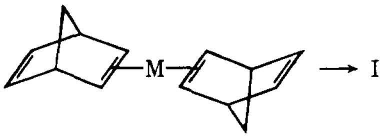
Possible pathways by which the photoexcited ClCu-NBD complex can yield Q are depicted in Scheme II. In path A the initially populated charge-transfer excited state or (following intersystem crossing) its corresponding triplet is sufficiently reactive to undergo direct conversion to Q. In path B the charge-transfer state is nonreactive and relaxes, either directly or via its triplet, to a π-π^* triplet state largely localized on NBD. The latter state is reported to undergo efficient conversion to Q.[42,43] The main role of Cu(I) in both A and B is to facilitate the absorption of 313-nm light by the otherwise

Scheme II



weakly absorbing olefin. Alternatively, in path C the excited complex undergoes transformation to a carbenium ion intermediate, II, containing a σ-bonded Cu(I). This species can rearrange to III, which subsequently collapses to Q. Such "photocupration" has been proposed[4] as a possible key step in the copper catalysis of olefin photoreactions. The absence of a noticeable solvent effect upon the quantum yield (Table II), however, does not seem consonant with an intermediate involving any significant degree of charge separation.

Finally, the specificity of Q production in the presence of CuCl is striking in view of the numerous examples[10-12] of transition metal catalyzed thermal and photochemical cycloadditions of NBD. The pronounced dependence of the product distribution on the nature of the catalyst suggests that such processes are intramolecular, involving the intermediacy of metal–NBD complexes. Thus the template effect of the metal in binding two (or more) NBD molecules in close proximity facilitates the formation of addition products (an example is given in eq 8):



(8)

The absence of significant photodimerization of NBD in the presence of CuCl is in accord with our earlier suggestion that ClCu–NBD is the only complex formed in appreciable concentration. The minimal dimerization observed in neat NBD suggests that ClCu–$(NBD)_2$ formation is inconsequential even under these forcing conditions. Small values of the formation constant are, in fact, expected for 1:2 CuCl–olefin complexes, since the strongly associating chloride ion effectively competes with the olefin for coordination sites on Cu(I).[30c,44] The presence of such competition is also consistent with our observation that NBD is displaced from ClCu–NBD by low concentrations of added Cl^- (eq 6).

Acknowledgment. This investigation was supported by the Energy Research and Development Administration through Contract No. E(38-1)-893 and the National Science Foundation through Grant No. MPS75-13752. The authors thank Dr. Paul Grutsch for valuable technical assistance.

References and Notes

(1) W. Strohmeier and G. Csontos, *J. Organomet. Chem.*, **72**, 277 (1975).
(2) S. N. Aliwi and C. H. Bamford, *J. Chem. Soc., Faraday Trans.*, **71** (1), 52 (1975).
(3) M. S. Wrighton, G. S. Hammond, and H. B. Gray, *J. Organomet. Chem.*, **70**, 283 (1974).
(4) R. G. Salomon and M. F. Salomon, *J. Am. Chem. Soc.*, **98**, 7454 (1976).
(5) M. S. Wrighton, G. S. Hammond, and H. B. Gray, *J. Am. Chem. Soc.*, **93**, 3285 (1971).
(6) Details of the mechanism will vary depending upon the specific system considered. For example, one or more of the steps will generally be irreversible.
(7) M. S. Wrighton, *Chem. Rev.*, **74**, 401 (1974).
(8) C. Kutal, D. P. Schwendiman, and P. Grutsch, *Sol. Energy*, **19**, in press.
(9) (a) D. P. Schwendiman and C. Kutal, *Inorg. Chem.*, **16**, 719 (1977). (b) Two earlier reports of this process have appeared; however, no quantitative photochemical results were obtained in either study. D. J. Trecker, R. S. Foote, J. P. Henry, and J. E. McKeon, *J. Am. Chem. Soc.*, **88**, 3021 (1966); (c) R. Srinivasan, U.S. Patent 3 350 291 (1967) (*Chem. Abstr.* **68**, 77855u (1968)).
(10) G. N. Schrauzer, *Adv. Catal.*, **18**, 373 (1968).
(11) A. R. Fraser, P. H. Bird, S. A. Bezman, J. R. Shapley, R. White, and J. A. Osborn, *J. Am. Chem. Soc.*, **95**, 597 (1973).
(12) B. Hill, K. Math, D. Pillsbury, G. Voecks, and W. Jennings, *Mol. Photochem.*, **5**, 195 (1973).
(13) C. D. Smith, *Org. Synth.*, **51**, 133 (1971).
(14) A. J. Gordon and R. A. Ford, "The Chemist's Companion", Wiley, New York, N.Y., 1972.
(15) G. Brauer, "Handbook of Preparative Inorganic Chemistry", 2nd ed, R. F. Riley, Translation Ed., Academic Press, New York, N.Y., 1963.
(16) H. L. Haight, J. R. Doyle, N. C. Baenziger, and G. F. Richards, *Inorg. Chem.*, **2**, 1301 (1963).
(17) D. A. Edwards and R. Richards, *J. Chem. Soc., Dalton Trans.*, 2463 (1973).
(18) The slight coloration suggests the presence of Cu(II) impurities. The extreme air and moisture sensitivity of this compound made its handling very difficult.
(19) D. A. Edwards and R. Richards, *J. Organomet. Chem.*, **86**, 407 (1975).
(20) J. A. Bertrand and R. I. Kaplan, *Inorg. Chem.*, **5**, 489 (1966).
(21) D. R. Arnold, D. J. Trecker, and E. B. Whipple, *J. Am. Chem. Soc.*, **87**, 2596 (1965).
(22) F. G. Moses, R. S. H. Liu, and B. M. Monroe, *Mol. Photochem.*, **1**, 245 (1969).
(23) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).
(24) R. Srinivasan, *J. Am. Chem. Soc.*, **86**, 3318 (1964); a saturated CuCl solution in ether has an extinction coefficient of $\sim 80\ M^{-1}\ cm^{-1}$ at 297 nm and $\sim 10\ M^{-1}\ cm^{-1}$ at 250 nm.
(25) H. A. Benesi and J. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).
(26) A value of $\epsilon_{300nm} = 8.7 \times 10^2\ M^{-1}\ cm^{-1}$ is calculated from the linear least-squares intercept of this line, while the intercept/slope ratio defines a lower limit of $\sim 10^2$ for the overall equilibrium constant for complex formation.
(27) R. G. Salomon and J. K. Kochi, *J. Am. Chem. Soc.*, **96**, 1137 (1974).
(28) Control experiments indicate that irradiation of NBD at 313 nm in the absence of cuprous salts affords no Q. Likewise, the thermal isomerization process is negligibly slow at ambient temperature.
(29) I. M. Kolthoff and J. F. Coetzee, *J. Am. Chem. Soc.*, **79**, 1852 (1957).
(30) We consider it unlikely that a significant amount of the 2:1 complex, $(CuCl)_2$–NBD, exists in solution in the presence of a large excess of NBD, since such behavior would require that CuCl preferentially adds to ClCu–NBD rather than to uncoordinated NBD. This preference is not observed, for example, in unsubstituted diolefin complexes of Ag^+: (a) S. Winstein and H. J. Lucas, *J. Am. Chem. Soc.*, **60**, 836 (1938); (b) J. G. Traynham and J. R. Olechowski, *ibid.*, **81**, 571 (1959). While evidence for a $(Cu^+)_2$–NBD species in solution has been reported, the NBD/Cu ratio employed (~ 1) was considerably lower than in the present study. (c) R. G. Salomon and J. K. Kochi, *ibid.*, **95**, 1889 (1973).
(31) J. M. Harvilchuck, D. A. Aikens, and R. C. Murray, Jr., *Inorg. Chem.*, **8**, 539 (1969). Similarly, it was concluded that the equilibrium constant for 1:2 complex formation in the analogous Cu^+–norbornene system is "not *very* large".[27]
(32) R. A. Zelonka and M. C. Baird, *J. Organomet. Chem.*, **33**, 267 (1971).
(33) In contrast, complexes of several other low valent transition metals are known to effectively catalyze the Q to NBD reversion reaction: K. C. Bishop, *Chem. Rev.*, **76**, 461 (1976).
(34) S. E. Manahan and R. T. Iwamoto, *J. Electroanal. Chem.*, **13**, 411 (1967).
(35) D. J. Trecker, J. P. Henry, and J. E. McKeon, *J. Am. Chem. Soc.*, **87**, 3261 (1965).
(36) J. C. Rapean and P. V. Shaw, U.S. Patent 3 860 497 (1975); (*Chem. Abstr.*, **82**, P139523*i* (1975)).
(37) Any inhibitor originally present in the commercially available NBD employed in this study would undoubtedly be removed during our purification procedure.
(38) N. C. Baenziger, H. L. Haight, and J. R. Doyle, *Inorg. Chem.*, **3**, 1535 (1964).
(39) In the gas phase, olefin-to-metal charge transfer is energetically much more favorable than the reverse transition. It is uncertain whether this situation persists in solution, however, due to the unknown contribution of solvation energy which preferentially stabilizes metal to olefin charge transfer: H. Hosoya and S. Nakagura, *Bull. Chem. Soc. Jpn*, **37**, 249 (1964). This question is currently being studied in our laboratory.
(40) The highest occupied Huckel π-molecular orbital (HOMO) in NBD features a bonding interaction between C_1–C_2 and C_3–C_4 and an antibonding interaction between C_1–C_3 and C_2–C_4. Conversely, the lowest unfilled π-molecular orbital (LUMO) is antibonding between C_1–C_2 and C_3–C_4, but bonding between C_1–C_3 and C_2–C_4.[9a] Thus the removal of electron density from HOMO (charge transfer to metal) or the addition of electron density to LUMO (charge transfer to ligand) produces the bond weakening–strengthening effects noted.
(41) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed, Wiley, New York, N.Y., 1972, chapter 23.
(42) S. Murov and G. S. Hammond, *J. Phys. Chem.*, **72**, 3797 (1968).
(43) J. W. F. van Ingen, C. H. C. van Tieghem, and W. A. Cramer, *J. Chem. Phys.*, **53**, 3665 (1970).
(44) S. E. Manahan, *Inorg. Chem.*, **5**, 2063 (1966).