CH^{a}H^{b}P$_2$ protons proves that inversion of the A frame is slow on the NMR time scale. Anal. Calcd C, 42.8; H, 3.5; F, 7.8; P, 10.6. Found: C, 42.7; H, 3.4; F, 7.9;, P, 10.6.

Another similar reaction was monitored by ^{31}P NMR spectroscopy. This showed that while significant reaction occurred after 1 h, substantially complete reaction required 24 h. The formation of a number of unidentified minor phorphous-containing impurities was revealed as well as the formation of some [Pt(dppm)$_2$]$^{2+}$ cation (δ -59 m). This was confirmed by treatment of the solution with excess of aqueous KPF$_6$ when [Pt(dppm)$_2$][PF$_6$]$_2$ (11% based on platinum), identified by its infrared spectrum, was precipitated. After this treatment the reaction solution no longer exhibited the resonance at -59 ppm but was otherwise unchanged.

Treatment of [Pt$_2$Me(dppm)$_3$][PF$_6$] with Iodomethane in Benzene. Iodomethane (0.23 g, 1.50 mmol) was added to a suspension of [Pt$_2$Me(dppm)$_3$][PF$_6$] (0.060 g, 0.035 mmol) in benzene (3 mL) and stirred at 20 °C for 5 h. The yellow solid was recovered by filtration, was washed with benzene, and was found (infrared) to be unchanged starting material (0.054 g, 90%).

Kinetic Studies.[11] Solutions of [Pt$_2$H(μ-H)(Me(μ-dppm)$_2$][SbF$_6$] (1 mL, 7.71 × 10^{-4} M) and dppm (2 mL, 7.20 × 10^{-3} M) were mixed and diluted to a volume of 10 mL. Part of this solution was added to a 1-cm quartz cuvette held in the cell compartment (thermostated with circulating water to 25 °C) of a Cary spectrophotometer. Spectra (450–300 nm) were recorded at suitable intervals until no further change occurred. A graph of ln [$A_\infty - A$] vs. time, where A is the absorbance at 330 nm, gave a good straight line plot from which the first-order rate constant, k_{obsd} was calculated. The same method was used for reactions with PPh$_3$.

Variable-Temperature NMR Studies.[11] Triphenylphosphine (0.77 mmol) was added to a solution of [Pt$_2$H(μ-H)Me(μ-dppm)$_2$][SbF$_6$] (0.077 mmol) in CD$_2$Cl$_2$ (0.50 mL) in an NMR tube cooled to -78 °C. After dissolution of the PPh$_3$ at -78 °C, the tube was added to the probe (precooled to -90 °C) of a Varian XL100 NMR spectrometer. The ^{1}H NMR spectrum was recorded, and further spectra were recorded at higher temperatures (Table III) until reaction to give H$_2$ and methyldiplatinum(I) complex was significant. The variable-temperature ^{31}P{^{1}H} NMR spectra were obtained in a similar way but with a Varian XL200 NMR spectrometer.

A similar experiment was carried out by using PPh$_3$ (1.5 × 10^{-4} mol) and [Pt$_2$(μ-H)Me$_2$(μ-dppm)$_2$][PF$_6$] (0.66 × 10^{-4} mol) in CD$_2$Cl$_2$ (1.3 mL). ^{1}H and ^{31}P{^{1}H} NMR spectra from -90 to 0 °C showed only signals due to the reagents, with no evidence for complex formation.

Acknowledgment. We thank NSERC (Canada) and Imperial Oil Ltd. for financial support (R.J.P.) and SERC (UK) for the award of a postdoctoral research assistantship (A.Y.).

Registry No. Ia, 84190-20-5; Ib, 84190-22-7; Ic, 84190-23-8; Id, 84190-06-7; Ie, 84190-25-0; II, 89378-06-3; [Pt$_2$Me(CO)(μ-dppm)$_2$][SbF$_6$], 89378-02-9; [Pt$_2$Me$_2$(μ-I)(μ-dppm)$_2$][PF$_6$], 89378-04-1; [Pt(dppm)$_2$][PF$_6$]$_2$, 72950-65-3; [Pt$_2$(dppm)$_3$], 69152-81-4; [Pt(PPh$_3$)$_4$], 14221-02-4; MeI, 74-88-4.

Photoisomerization of *cis*,*cis*-1,5-Cyclooctadiene in the Presence of Copper(I) Complexes: Wavelength Dependence

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Received December 19, 1983

Irradiation of [CuCl(cc-1,5-COD)]$_2$ or Cu(acac)(cc-1,5-COD) in the presence of an excess of cc-1,5-COD in methanol catalytically gave ct-1,5-COD as the exclusive product at wavelengths >290 nm and TCO plus minor amounts of tt-1,5-COD at wavelengths >240 nm. Cu(acac)(cc-1,5-COD) was generated in situ by photoreduction, electrolysis, or metathesis under appropriate conditions. Sparingly soluble [CuCl(ct-1,5-COD)]$_2$ was isolated and identified as the immediate intermediate in the photorearrangement to TCO. The stoichiometric interconvertibility between [CuCl(cc-1,5-COD)]$_2$ and [CuCl(ct-1,5-COD)]$_2$ by >290-nm irradiation was established from the presence of an isosbestic point in UV spectra. A definite mechanism was proposed to account for the rearrangements.

Aromatic ketones with high triplet state energy (e.g., xanthone, benzophenone, acetophenone, etc.) sensitize the photoreduction of bis(acetylacetonato)copper(II), Cu(acac)$_2$, in hydrogen atom donating solvents, such as methanol or tetrahydrofuran, to give copper (I) complexes.[1-4] Kinetic and mechanistic investigations show that the primary photoreaction is the electron transfer from Cu(acac)$_2$ to triplet-state ketones and that the hydrogen-transfer step determines the overall efficiency of the photoreduction.[3] The proposed reaction pattern is summarized below, where L represents appropriate ligands:

$$\mathrm{Cu(acac)_2 + Ph_2CO \overset{h\nu}{\rightleftharpoons} Cu(acac)^+ + acac\cdot + Ph_2CO^{-}\cdot}$$

$$\mathrm{Cu(acac)^+ + Ph_2CO^{-}\cdot + \mathit{x}L \rightarrow Cu(acac)L_{\mathit{x}} + Ph_2CO}$$

$$\mathrm{2acac\cdot + CH_3OH \rightarrow 2acacH + CH_2O}$$

It is also well-known that in the presence of copper(I) complexes, olefins undergo photoreactions involving rearrangements, cycloadditions, and fragmentations.[5,6] Among them, the cuprous chloride catalyzed photorearrangement[7-11] of *cis*,*cis*-1,5-cyclooctadiene (cc-1,5-COD) to

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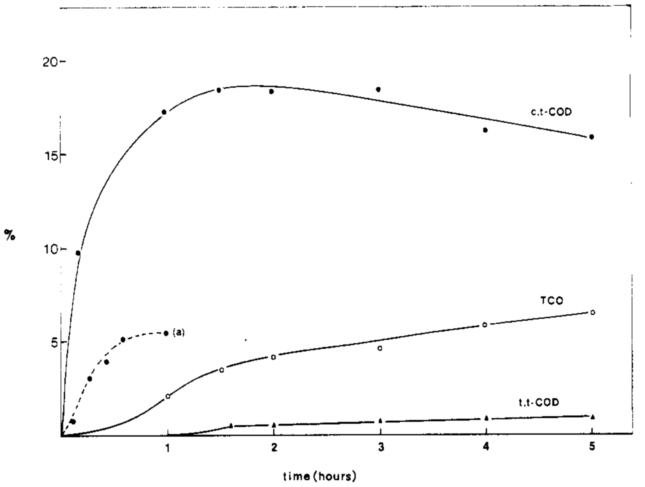

Figure 1. The percentage variation of products during photolysis (low-pressure Hg lamp, 254 nm) of a methanol solution containing [CuCl(cc-1,5-COD)]$_2$ (2 mmol) and cc-1,5-COD (4 mmol); curve a represents percent of ct-1,5-COD in solution; others, those in total mixtures.

tricyclo[3.3.0.0^{2,6}]octane (TCO) was originally reported by Srinivasan,[7] and its mechanism has been extensively studied by various groups. Evidence was provided that both *cis,trans*-1,5-cyclooctadiene (ct-1,5-COD) and *trans,trans*-1,5-cyclooctadiene (tt-1,5-COD) are the intermediates in the photorearrangement[8] and that the latter readily photorearranges to TCO from its free state.[8] A separate study shows that intermolecular hydrogen transfer may be required in the photorearrangement owing mainly to the observation of the loss of labeled deuterium in TCO.[10] More recently, studies by UV spectroscopy show that [CuCl(cc-1,5-COD)]$_2$ is the primary light-absorbing species, excitation of which triggers the photorearrangement.[11]

We report some direct experimental evidence that leads to a definite mechanistic proposal on the light-induced rearrangements of copper(I)–COD complexes.

Results and Discussion

CuCl-Catalyzed Photoisomerizations. [CuCl(cc-1,5-COD)]$_2$ is more soluble in methanol than in hydrocarbon solvents, and its methanol solution is much more stable toward air oxidations than that of Cu(acac)(cc-1,5-COD) (vide infra). A methanol solution of this complex exhibited λ_{max} at 246 nm and a shoulder at ca. 290 nm which tailed above 300 nm. Irradiation of a mixture of [CuCl(cc-1,5-COD)]$_2$ and an excess of cc-1,5-COD in methanol through a Pyrex filter caused a prolific formation of a white precipitate in several minutes; sometimes the precipitation occurred suddenly after a short irradiation period. GC analysis of the solution, however, gave only the cc-1,5-COD peak without a trace of other isomers even after a 4-h irradiation. The solid was obviously CuCl complexes that were decomposed by ammonia to give cc-1,5-COD (70%) and ct-1,5-COD (28%) without a trace of tt-1,5-COD.

Irradiation of similar mixtures in methanol with a 254-nm light source gave a heavy white precipitate in several minutes, the formation of which caused the abrupt drop in the percent yield of ct-1,5-COD in solution. The GC analysis of the total mixtures (solid and solution) showed that a large quantity of COD existed as insoluble CuCl complexes and that the formation of TCO commenced only after an induction period (Figure 1). A small amount (<2%) of tt-1,5-COD started to emerge after 60 min of irradiation, indicating that this compound was not a mandatory precursor to TCO, though it could be rearranged to TCO by photolysis.[8] When a medium-pressure lamp and a Corex filter were used, the pattern of the product formation was different from that in Figure 1; TCO was formed more rapidly and ct-1,5-COD maintained lower percentages during photolysis. Preparatively up to 90% of TCO was obtained when [CuCl(cc-1,5-COD)]$_2$ (0.75

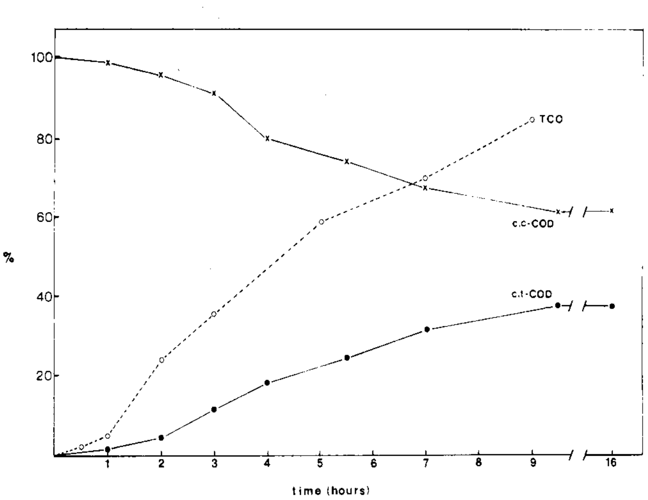

Figure 2. The percentage variation of cc-1,5-COD (x) and ct-1,5-COD (●) during photolysis (Pyrex filter) of Cu(acac)$_2$ (2.8 mmol), benzophenone (4 mmol), and cc-1,5-COD (25 mmol) in methanol (150 mL). The broken line shows the formation of TCO (O) in the irradiation of (Corex filter) cc-1,5-COD (4.8 mmol) and [CuCl(cc-1,5-COD)]$_2$ (0.75 mmol) in methanol (110 mL).

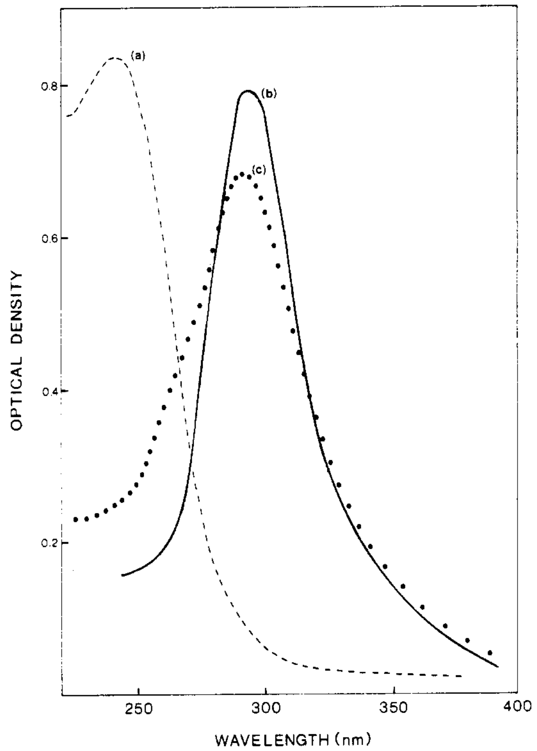

Figure 3. The UV absorption spectra (in ether) of (a) [CuCl(cc-1,5-COD)]$_2$ (2.76 × 10^{-4} M), (b) [CuCl(ct-1,5-COD)]$_2$ (4.5 × 10^{-4} M) prepared from CuCl and respective COD, and (c) the precipitate obtained from the photolysis of the former and cc-1,5-COD in methanol.

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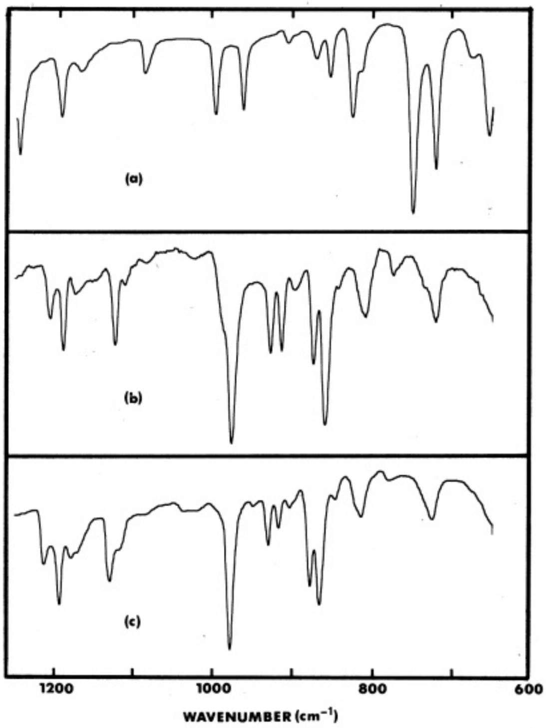


Figure 4. The IR spectra (Nujol) of (a) [CuCl(cc-1,5-COD)]$_2$, (b) the precipitate obtained from the photolysis of this complex and cc-1,5-COD in methanol, and (c) [CuCl(ct-1,5-COD)]$_2$ prepared from CuCl and ct-1,5-COD.

mmol) and cc-1,5-COD (4.8 mmol) in methanol were photolyzed with a Corex filter for 9 h (see Figure 2). Interruption of the above photolysis at 30 min gave the precipitate in 88% yield containing 76% of ct-1,5-COD. The precipitate exhibited the IR and UV absorptions of an authentic solid prepared from ct-1,5-COD and CuCl in methanol (see Figures 3 and 4) in addition to those due to [CuCl(cc-1,5-COD)]$_2$.

The authentically prepared CuCl complex of ct-1,5-COD is stable in ether solution or in the solid state and gave only ct-1,5-COD on decomposition. Washings with cold methanol or pentane caused decreases in percent of C and H analysis, but the C/H ratio was correct for C_8H_{12}; similar phenomena[8] were observed for [CuCl(cc-1,5-COD)]$_2$ and indicated the lability of COD ligands. A methanol solution of the solid was stable under nitrogen but slowly oxidized in air to give green precipitates. Whereas the definite structure of the solid remained unknown, its molecular formula must be [CuCl(ct-1,5-COD)]$_2$ in view of the presence of mass spectral peaks above m/e 400. In solution these two COD complexes are also in dimeric forms as demonstrated by UV spectroscopic studies[11] and by the quantitative photolytic study (see Figure 6). It was suspected that the 1:1 heterogeneous complex [CuCl(cc-1,5-COD)][CuCl(ct-1,5-COD)] might be present in small amounts in the precipitates obtained from photolysis. Careful studies by computer-assisted subtraction of IR spectra of these photolytic precipitates (the ratios of the two COD varying from 4:1 to 1:4 by GC) always gave a sharp absorption at 993 cm^{-1}. This peak very likely arises from the 1:1 complex, but if it is, its amount is very small judging from the peak intensity.

In contrast to the fair solubility of [CuCl(cc-1,5-COD)]$_2$ in methanol and ether ($\approx 10^{-3}$ M), [CuCl(ct-1,5-COD)]$_2$ is sparingly soluble in methanol ($<10^{-5}$ M) and in ether (4.5×10^{-4} M). This low solubility in methanol caused the pattern of the product formation to be somewhat erratic and different from those observed in ether. Photolysis of a suspension of [CuCl(ct-1,5-COD]$_2$ in methanol through a Corex filter showed, by GC analysis of the substrate, that cc-1,5-COD and TCO but not tt-1,5-COD were formed (Figure 5); the formation of TCO was slow but steady. Similar irradiation through a Pyrex filter gave cc-1,5-COD rapidly but no TCO or tt-1,5-COD even after 2 h; only after 3 h of irradiation <1% of TCO was detected. Stoichiometric interconvertibility of [CuCl(cc-1,5-COD)]$_2$ and [CuCl(ct-1,5-COD)]$_2$ induced by >290-nm light was demonstrated by the presence of the isobestic point at 268 nm when photolysis of an ether solution of the former was monitored by UV spectroscopy (Figure 6). Irradiation beyond 11 min approached a photostationary state. It is pertinent to mention that the UV absorption curves of these CuCl–COD complexes are concentration dependent

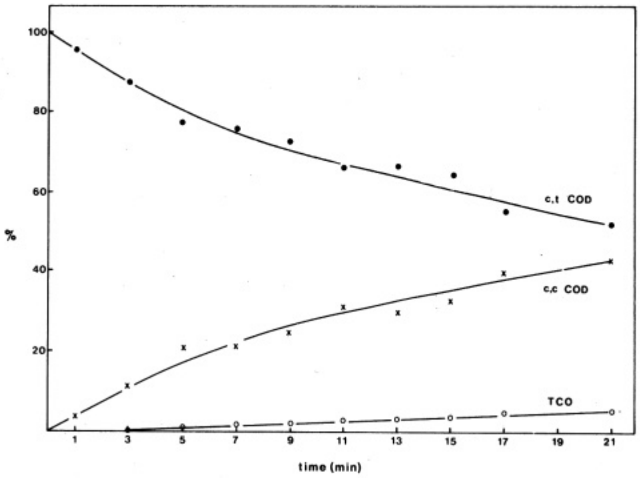


Figure 5. The percentage variation of ct-1,5-COD (●), cc-1,5-COD (x), and TCO (○) during photolysis of [CuCl(ct-1,5-COD)]$_2$ in methanol through a Corex filter.

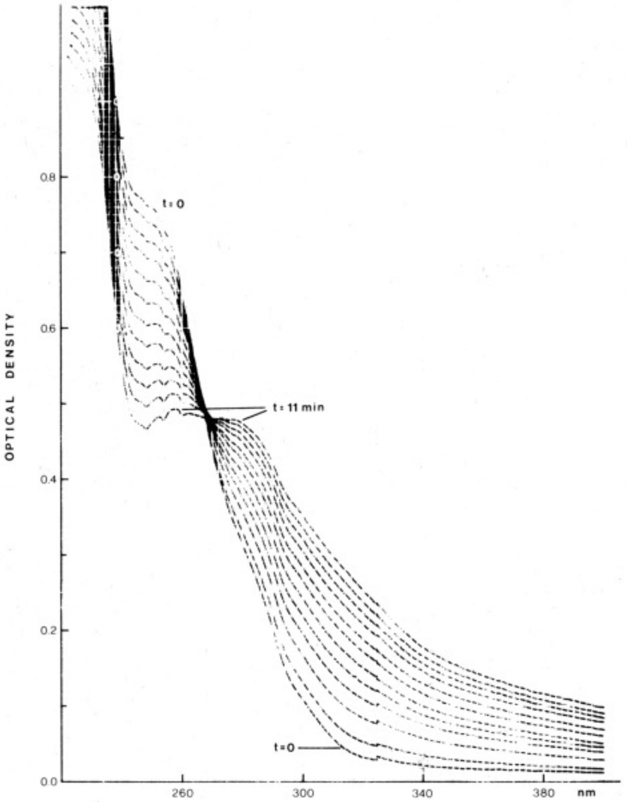


Figure 6. The UV traces of the photolysis of [CuCl(cc-1,5-COD)]$_2$ (1.20×10^{-3} M in ether, 1 cm cell) through a Pyrex filter; each curve was recorded after consecutive 1-min irradiations.

(compare Figures 3 and 6), obviously arising from dissociations of the complexes in solution.[8] Because of the absence of an excess of COD, these experiments do not exactly represent the product formation pattern of the catalytic isomerizations; they do indicate TCO is formed directly from the light-induced reaction of [CuCl(ct-1,5-COD)]$_2$. However, the product formation patterns (e.g., Figure 1) suggest that the direct photorearrangement from [CuCl(cc-1,5-COD)]$_2$ to TCO by the 240–290-nm excitation is unlikely.

It was also shown that benzophenone did not sensitize CuCl–COD complex isomerizations but, instead, slowed them down by internal filter effects. In these attempts, the oxetanes derived from benzophenone and COD were obtained in good yields.

Cu(acac)-Catalyzed Photoisomerizations. Irradiation of a methanol solution of Cu(acac)$_2$ and benzophenone in the presence of a large excess of cc-1,5-COD under nitrogen through a Pyrex filter caused bleaching of the solution. GC analysis of organic extracts taken during the reaction showed that ct-1,5-COD was formed at the expense of cc-1,5-COD and reached a photostationary state with a ratio of 38:62 in 7–8 h. As the amount of ct-1,5-COD that can be found is nearly 10 times the amount of Cu(acac)$_2$ initially present, the photoisomerization is a catalytic process. At about this time precipited metallic copper blocked the light path and had to be removed to permit further irradiation. The photolysate contained benzophenone and acetylacetone but no oxetane derived from the addition to 1,5-COD; tt-1,5-COD was not detected by GC analysis. As the bleached solution reacted with triphenylphosphine readily to give Cu(acac)(Ph$_3$P)$_2$, a copper(I) complex, Cu(acac)(cc-1,5-COD), is probably formed in analogy to the copper(I) complex formations in our previous studies.[1,2] This copper(I) complex, when left in the methanol solution overnight, slowly disproportionated to form Cu(acac)$_2$ and copper metal; the isolation of the copper(I) complex was not attempted. On the basis of the previous studies, the following reaction sequence is proposed:

$$\mathrm{Ph_2CO} \xrightarrow{h\nu} {}^1[\mathrm{Ph_2CO}] \rightarrow {}^3[\mathrm{Ph_2CO}] \qquad (1)$$

$$^3[\mathrm{Ph_2CO}] + \mathrm{Cu(acac)_2} \rightarrow \mathrm{Ph_2CO} + \mathrm{Cu(acac)} + \mathrm{acac}\cdot \qquad (2)$$

$$\mathrm{Cu(acac)} + \text{cc-1,5-COD} \rightarrow \mathrm{Cu(acac)(cc\text{-}1,5\text{-}COD)} \qquad (3)$$

$$2\mathrm{Cu(acac)(cc\text{-}1,5\text{-}COD)} \rightarrow \mathrm{Cu(acac)_2} + \mathrm{Cu(0)} + 2\,\text{cc-1,5-COD} \qquad (4)$$

The generation and reaction of acetylacetonyl radical with alcohol[1] and olefins[4] have been demonstrated.

Control experiments showed that cc-1,5-COD did not isomerize when photolyzed in the presence of Cu(acac)$_2$ or of benzophenone alone; in the latter case only the oxetanes derived from photoaddition of benzophenone to COD were obtained. The induction period at the beginning of irradiation as shown in Figure 2 is strongly indicative of the fact that the intermediary Cu(acac)(cc-1,5-COD), formed during the sensitized photoreduction, is the species catalyzing the light-induced COD isomerization: this is also supported by the following experiments.

The investigation of electrolytic reduction of Cu(acac)$_2$ in methanol by cyclic voltammetry showed that the reduction potentials occurred at $E_{1/2} = -0.37$ V and $E_{1/2} = -0.63$ V (vs. SCE, Kacac the supporting electrolyte), corresponding to Cu(acac)$_2$/Cu(acac) and Cu(acac/Cu(0), respectively. During electrolysis in the presence of cc-1,5-COD (eq 5), the cathode solution turned yellowish but the solution in the anode compartment remained blue.

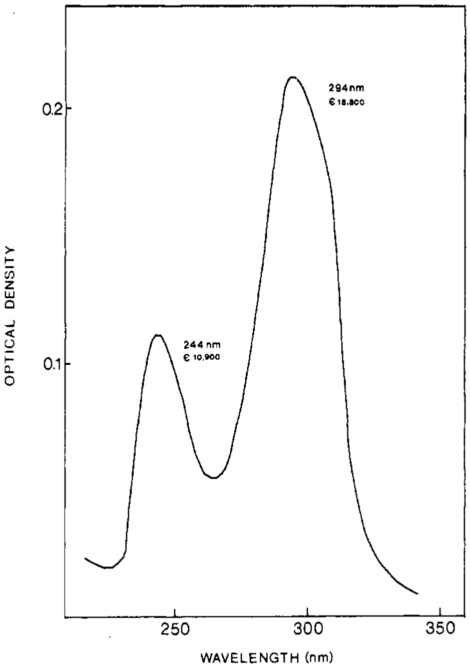
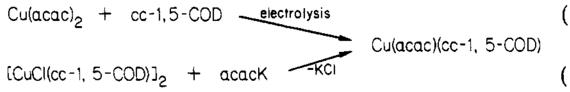


Figure 7. The UV spectrum of Cu(acac)(cc-1,5-COD) (10^{-5} M) in methanol prepared from [CuCl(cc-1,5-COD)]$_2$ and Kacac solutions under nitrogen at 0 °C.

Subsequently, a large-scale electrolysis of Cu(acac)$_2$ in the presence of cc-1,5-COD under argon and irradiation of the cathode compartment were carried out simultaneously. The sample from the cathode compartment was analyzed by GC to give ct-1,5-COD; owing to the rapid formation of metallic copper on the wall and the solution, the yield did not exceed 5%.



(5)

(6)

Alternatively, the metathesis of [CuCl(cc-1,5-COD)]$_2$ with potassium acetylacetonate in methanol under nitrogen precipitated potassium chloride as a white solid and gave a colorless solution (eq 6). The solution was instantly oxidized to the blue solution of Cu(acac)$_2$ by the air but turned to blue with deposition of copper metal very slowly under nitrogen. The phenomena were similar to those observed with the complexes of Cu(acac) previously.[1] The solution showed UV absorption at $\lambda_{\max}$ 294 and 244 nm (Figure 7) and, presumably, contained Cu(acac)(cc-1,5-COD), the disproportionation of which in the presence of excess cc-1,5-COD under nitrogen was much slower. However, cc-1,5-COD was not isomerized when kept in the dark. Irradiation of the solution right after the mixing, either after removal of potassium chloride or without the removal, through a Pyrex filter under nitrogen gave ct-1,5-COD. During the photolysis a small amount of black precipitate was formed and copper metal slowly deposited on the wall, retarding the photoreaction. Under the conditions a photostationary state was obtained in about 90 min to give ct-1,5-COD (26%) and cc-1,5-COD (73%) but no tt-1,5-COD and TCO as shown by GC analysis.

When a similarly prepared solution was irradiated with a Corex filter, the percentage of TCO increased steadily but slowed down in 4 h (to ca. 6%) due to the coating of the probe by copper metals. Only <1% of ct-1,5-COD was detected in the later stage. Under similar conditions, if benzophenone was added to the solutions, the formations of ct-1,5-COD (with Pyrex filter) and TCO (with Corex filter) were both severely retarded. In both cases, the oxetanes derived from photoaddition of triplet benzophenone to COD were obtained. In spite of its ability to promote the photoreduction of $\mathrm{Cu(acac)_2}$, these results indicate that triplet benzophenone neither interacts with the copper(I) complex nor sensitizes the photorearrangement but undergoes simple photoaddition to COD.

Photolysis of bis(hexafluoroacetylacetonato)copper(II), $\mathrm{Cu(hfac)_2}$ and benzophenone through a Pyrex filter in methanol in the presence of cc-1,5-COD also caused the similar photoreduction of the copper(II) complex and the isomerization of COD with less efficiency. Presumably, Cu(hfac)(cc-1,5-COD) was the catalytic species in the light-induced isomerization of COD. However, $\mathrm{Cu(acac)(PPh_3)_2}$, a stable copper(I) complex, did not catalyze the photoisomerization of COD when its methanol solution was irradiated in the presence of cc-1,5-COD. The failure is attributed to the inability of 1,5-COD to replace the triphenylphosphine ligands to form a copper(I)–1,5-COD complex since copper(I)–phosphine coordination is known to be fairly strong.

Photoisomerization Mechanisms. Summarizing the results described here and in the previous reports, a definite mechanism for copper(I) complex catalyzed photoisomerization of 1,5-COD can be proposed as in eq 7–10.

$$\text{CuX} + \text{cc-1,5-COD} \rightleftarrows \text{CuX(cc-1,5-COD)} \qquad (7)$$

$$\text{CuX(cc-1,5-COD)} \xrightarrow{\lambda > 290\ \text{nm}} \text{CuX(ct-1,5-COD)} \qquad (8)$$

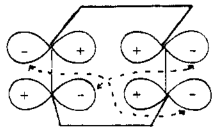
$$\text{CuX(ct-1,5-COD)} \xrightarrow[\lambda\ 240\text{–}290\ \text{nm}]{} \text{CuX(tt-1,5-COD)} + \text{TCO} + \text{CuX} \qquad (9)$$

$$\text{CuX(ct-1,5-COD) or CuX(tt-1,5-COD)} + \text{cc-1,5-COD} \rightleftarrows \text{CuX(cc-1,5-COD)} + \text{ct-1,5-COD or tt-1,5-COD} \qquad (10)$$

The monomeric form of copper(I) complexes are used to write the generalized mechanism with an understanding that certain complexes are actually in the dimeric form.

The photorearrangement of $\mathrm{[CuCl(ct\text{-}1,5\text{-}COD)]_2}$ to TCO and the failure of $\mathrm{[CuCl(cc\text{-}1,5\text{-}COD)]_2}$ to do the same by 240–290-nm irradiation as well as the wavelength dependency of the photorearrangement patterns pose interesting mechanistic questions. For concerted rearrangements, in theory,[12] the crossed [2 + 2] cycloaddition of ct-1,5-COD to TCO is stereochemically feasible only by a supra/antara mode, and that of cc-1,5-COD to TCO only by the supra/supra mode. According to the frontier orbital theory,[12] the former is allowed to occur from the ground state as in 1 while the latter is from an excited state as in 2.

1



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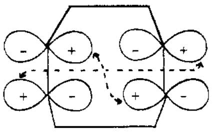

Therefore, the coordination of ct-1,5-COD with the copper(I) metal center must perturb orbital symmetry to the opposite array (i.e., to that shown in 2) so that photoexcitation of $\mathrm{[CuCl(ct\text{-}1,5\text{-}COD)]_2}$ can promote the symmetry properties to the correct array as in 1 to undergo the concerted supra/antara rearrangement to TCO. The wavelength dependency of the photorearrangement to TCO may be understood in terms of the attainability of the correct orbital symmetry as in 1 by the 240–290-nm excitation.

In the absence of proof for a concerted reaction, the photorearrangement can be satisfactorily explained by a nonconcerted process, for example, by a stepwise radical cyclization. The observation of $\mathrm{[CuCl(ct\text{-}1,5\text{-}COD)]_2}$ to TCO by higher energy (240–290 nm) excitation but not by lower (>290 nm) energy excitation may be attributed to a purely energy supply and demand relation for the cyclization to strained TCO. That is, radiationless transition from an upper excited state should provide sufficient vibrational energy to overcome the activation energy needed for the uphill cyclization, while that from a lower excited state affords only enough energy to cause the cis–trans isomerization.

Conclusion

Kutal et al.[11] have provided viable arguments that in solutions of CuCl and cc-1,5-COD, $\mathrm{[CuCl(cc\text{-}1,5\text{-}COD)]_2}$ is the primary light-absorbing species, the excited state of which induces isomerization of cc-1,5-COD. Our results furnish a direct proof of this proposal; the only species absorbing light significantly above the Pyrex cutoff (290 nm) are CuX-(1,5-COD) complexes arising from the tailing of the absorption bands (see Figures 3 and 7). This excitation (>290 nm) causes the reversible cis–trans isomerization of cc-1,5-COD and ct-1,5-COD within the complexes but no cyclization to TCO. The same isomerization was also induced by 240–290-nm irradiation of CuX-1,5-COD complexes. For heterogeneous reactions, solubility as well as absorbancy of copper(I)–COD complexes play significant roles in determining the product-formation pattern.

The excitation of $\mathrm{[CuX(ct\text{-}1,5\text{-}COD)]_2}$ with 240–290-nm light causes isomerization of ct-1,5-COD mainly to TCO and cc-1,5-COD and inefficiently to tt-1,5-COD; this is the main pathway to TCO in the photoisomerization. The photorearrangement of tt-1,5-COD also gives TCO[8] but is a minor pathway, and that of $\mathrm{[CuCl(cc\text{-}1,5\text{-}COD)]_2}$ does not directly afford TCO. The wavelength dependency provides means to synthesize either ct-1,5-COD or TCO in excellent yields. The slow formation of TCO in the photorearrangement is traced to two reasons, namely, the efficient isomerization of ct-1,5-COD to cc-1,5-COD and the low solubility of $\mathrm{[CuX(ct\text{-}1,5\text{-}COD)]_2}$ in various solvents under the conditions. Finally, whereas triplet-state benzophenone sensitizes the photoreduction of $\mathrm{Cu(acac)_2}$ efficiently, it does not interact with the CuCl and Cu(acac) complexes of 1,5-COD.

Experimental Section

Equipment and Material. Infrared spectra were recorded with a Perkin-Elmer 599-B spectrophotometer, ultraviolet–visible spectra with a Cary 210 spectrophotometer, and NMR spectra with a Varian EM-360 at 60 MHz or a Brucker 400 at 400 MHz. GC–MS analysis was carried out on a Hewlett-Packard Model 5985 spectrometer coupled with a GC equipped with SE-30 capillary column (15 m × 0.28 mm). Gas chromatography was performed on a Varian 1400 (FID) or a Hewlett-Packard 5792A and a HP3390 integrator equipped with a OV-1 (Hewlett-Packard, 12.5 m × 0.20 mm) or SE-30 (J & W, 15 m × 0.28 mm) capillary columns.

A sample of cc-1,5-COD purified by distillation showed GC peaks (OV-1, 50–200 °C at 10 °C/min) at 6.42 (TCO, 1.4%), 8.43 (ct-1,5-COD, 0.4%), and 9.12 min (cc-1,5-COD). These impurities could be eliminated when distilled through a fractionating column (30 cm). TCO was prepared by the procedure of Srinivasan[7] as a sample of 70% purity admixed with cc-1,5-COD; ct-1,5-COD was prepared according to the procedure of Whitesides et al.[8] The latter sample in $\mathrm{CHCl_3}$ or MeOH solution slowly turned to a white turbid solution probably due to polymerization. In the crude product of the latter preparation, a GC peak higher than that of ct-1,5-COD and lower than that of cc-1,5-COD was recorded and was assigned to tt-1,5-COD in analogy to reported GC retention time.[8] A typical chromatogram obtained under the following

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[12] Fukui, K.; Fujimoto, H. In "Mechanisms of Molecular Rearrangement"; Thyagarajan, B. S., Ed.; Interscience; New York, 1968; Vol. 2, p 113.

conditions (the temperature at injector 150 °C, oven 60 °C isothermal, and FID detector 200 °C) was TCO t_R 2.9, ct-1,5-COD 4.10, tt-1,5-COD 4.50, and cc-1,5-COD 5.25 min.

$[CuCl(cc\text{-}1,5\text{-}COD)]_2$ was prepared as white crystals according to the method of van den Hende and Baird[13] and showed UV absorption maxima at 246 nm (ϵ 5100), 285 (sh, 2360) in methanol under nitrogen. See Figure 3a for the UV spectrum in ether and Figure 4a for the IR spectrum: MS (EI), *m/e* (%) 44 (49), 57 (40), 76 (100), 111 (60), 412 (25), 414 (45), 416 (20), 418 (2).

Photolysis. Method 1. A solution was placed in a Hanovia type immersion cell and irradiated under nitrogen through an appropriate filter. The light sources were either a Hanovia medium-pressure mercury lamp (200 W) in combination with appropriate filter or a Pen Ray low-pressure mercury lamp (10 W, Ultraviolet Products Inc.). The solution was withdrawn at intervals for analysis. The solution (1 mL) was mixed with water (2 mL) and ether (2 mL). The ether layer was separated and passed through a small column of silica gel. The filtrate was injected into the GC column. For the analysis of solid and solution, the total mixture was vigorously shaken to make an even mixture, 2 mL of which was diluted with concentrated ammonium hydroxide (4 mL) and ether (4 mL). To the blue solution was added sodium cyanide to make a colorless aqueous phase. The ether layer was separated for GC injections.

Method 2. A photolysis solution was prepared under nitrogen. This solution (5-mL portion) was placed in 10-mL test tubes. At intervals, one tube was removed for analysis of the solution and of the total mixture (solution and solid) by the same methods as above.

Sensitized Photolysis of $Cu(acac)_2$ in the Presence of cc-1,5-COD. A suspension of $Cu(acac)_2$ (750 mg, 2.87 mmol), cc-1,5-COD (2.65 g, 25 mmol), and benzophenone (750 mg, 4.12 mmol) in methanol (150 mL) was irradiated under nitrogen through a Pyrex filter by method 1. The blue solution gradually turned to a colorless solution, and after 6 h, copper metal began to deposit on the apparatus. The colorless solution exposed to the air rapidly turned to a blue solution, and on prolonged exposure the copper metal dissolved slowly.

During the photolysis, aliquots of the solution were worked up to give ether extracts. GC analysis by peak matching showed four peaks at 2.89, 3.87, 4.85, and 16.60 min for acetylacetone, ct-1,5-COD, cc-1,5-COD, and benzophenone, respectively. Benzophenone remained constant up to 15 h of photolysis, and the percentage yields of ct-1,5-COD and cc-1,5-COD were shown in Figure 1; their absolute yields after 10 h of photolysis were 10.4 and 14.6 mmol, respectively. The peak corresponding to tt-1,5-COD was not detected. In a similar experiment, to the bleached photolysate was added triphenylphosphine under nitrogen after irradiation was stopped. The solution was worked up as before[1] to give $Cu(acac)(Ph_3P)_2$; mp and mmp 176–179 °C.

In a separate experiment, $Cu(acac)_2$ (198 mg, 0.76 mmol) and benzophenone (198 mg, 1.09 mmol) in methanol (40 mL) were irradiated under the same conditions for 2 h to give a black precipitate with a small amount of copper metal. This mixture was stirred under nitrogen with cc-1,5-COD (2 mL) in the dark for 5 h. GC analysis of the solution showed only the peak of cc-1,5-COD.

Irradiation of a solution of cc-1,5-COD (450 mg) and benzophenone (460 mg) caused the formation of the oxetane (18%) and benzhydrol (22%) but no other product. The oxetane was isolated by recrystallization; MS, *m/e* 290 (M^+, 1.1%), 183 (100), 105 (52); IR 3100–3000, 1600, 1000 (s), 950 (s) cm^{-1}.

The solution of $Cu(acac)_2$ (10^{-3} M) and cc-1,5-COD (10^{-2} M) in methanol (100 mL) was irradiated under nitrogen through a Pyrex filter. The UV absorption at 630 nm did not decrease after 3 h of irradiation and cc-1,5-COD was not isomerized.

Electrolytic Reduction of $Cu(acac)_2$ and Photocatalysis of Cu(acac)(cc-1,5-COD). The electrolytic apparatus consists of a Pt sheet as the cathode, a Pt wire as the anode, and an Ag wire as the reference electrode. The electrode compartments were separated by sintered glass and the solutions were kept under an argon atmosphere.

A solution of $Cu(acac)_2$ (784 mg, 3 mmol), potassium acetylacetonate (4.1 g, 30 mM), and cc-1,5-COD (1 mL, 8.0 mmol) in methanol (200 mL) showed a reversible cyclic voltammetry curve with $E_{1/2}$ at –0.37 and –0.63 V vs. SCE. This solution was electrolyzed and photolyzed simultaneously at –1.099 V for 6 h (total 100 C) when the cathode solution turned to a yellow color and a trace amount of Cu(0) was deposited. The irradiation was carried out by placing a Hanovia 200-W lamp near the cathode compartment. At every hour interval, aliquots of the solution were analyzed as above. The percentage yields of ct-1,5-COD increased slowly, reaching to 5% at 6 h of irradiation. No other peak except that of cc-1,5-COD was obtained.

The solution on exposure to the air rapidly turned to a blue solution. At 4 h of irradiation, part of the solution was withdrawn and added to a methanol solution of triphenylphosphine under nitrogen. From this solution $Cu(acac)(PPh_3)_2$, mp 175–178 °C, was isolated. Further irradiation, without electrolysis, gave copper metal precipitate and blocked the incident light.

Cyclic voltammetry was carried out with $Cu(acac)_2$ (20 mM) and Kacac (150 mM) in methanol under argon and a SCE reference electrode, using P.A.R. Electrochemistry System Model 170 (Princeton Applied Research Corp., Princeton, NJ). The working electrode is a platinum microdisc and the counterelectrode a platinum wire.

Formation and Photolysis of Cu(acac)(cc-1,5-COD) in Methanol. Solutions of $[CuCl(cc\text{-}1,5\text{-}COD)]_2$ (10^{-3} M) and of potassium acetylacetonate (10^{-5} M) in methanol were prepared under nitrogen. In a 10-mm quartz curvette, 4.5 mL of the latter and 45 μL of the former were mixed under nitrogen at ice–water temperature to give a yellow solution: see Figure 7 for the UV spectrum. The solution turned to blue with copper metal precipitates in 24 h.

For photolysis, a solution of potassium acetylacetonate (276 mg, 2 mmol) and cc-1,5-COD (4.8 mmol) in methanol (20 mL), placed in a two-necked flask, was cooled in an ice-bath and stirred under nitrogen. $[CuCl(cc\text{-}1,5\text{-}COD)]_2$ (414 mg, 2 mmol) was added and the mixture was stirred for 5 min under these conditions. The mixture was filtered directly into a photocell containing methanol (80 mL) prepurged with nitrogen. During photolysis, samples were withdrawn at intervals and worked up as above for GC analysis.

Irradiation with a Pyrex filter started to give a small amount of a black precipitate, which increased slightly in 5 h. GC analysis showed that ct-1,5-COD built up slowly in the first period but increased rapidly in 60 min to reach 25% at a near stationary state. No tt-1,5-COD or TCO were detected. With use of a Corex filter, metallic copper started to coat the cold finger in 1 h and increased rapidly, but the solution remained pale yellow. After a 20-min induction period, TCO was formed rapidly. ct-1,5-COD was detected in the 1% range by GC analysis. Similar results were obtained when the starting materials were charged into the photocell without filtration and photolyzed.

[CuCl(cc-1,5-COD]-Catalyzed Photoisomerization of cc-1,5-COD. Corex Filter. To a methanol (110 mL) solution containing cc-1,5-COD (2 mmol) was added the CuCl complex (414 mg, 2 mmol) with stirring under nitrogen; a small amount of white solid was not dissolved. Upon irradiation, a large amount of white solid appeared in about 5 min. The samples were filtered through a sintered glass filter and worked up as usual for GC analysis. After a 5-min induction period TCO started to form and after 40 min tt-1,5-COD appeared: ct-1,5-COD formed immediately and remained at the 3–5% range.

After 70 min of irradiation, the samples of combined solution and solid were also analyzed by the following procedure. The suspension (2 mL), ether (4 mL), and concentrated ammonium hydroxide was shaken to give a blue aqueous layer. Sodium cyanide was added to decolorize the blue aqueous layer. The ether layer was separated, dried with Na_2SO_4, and analyzed by GC. Both the percentage of ct- and tt-1,5-COD remained almost constant at about 8–10% and 4–5% levels up to 12 h of irradiation. A similar experiment was run with a Pen Ray low-pressure mercury lamp as the light source (see Figure 1).

In a preparative run $[CuCl(cc\text{-}1,5\text{-}COD)]_2$ (310 mg, 1.5 mmol) and cc-1,5-COD (75 mmol) in methanol (110 mL) were photolyzed under nitrogen. In 5 h, a small amount of red copper metal deposited on the wall and increased. In 10 h, TCO was formed

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[13] van den Hende, J. H.; Baird, C., Jr. *J. Am. Chem. Soc.* **1963**, *85*, 1009.

in 89%. During photolysis, GC analysis at intervals showed that ct-1,5-COD and tt-1,5-COD were present in about 2.5% and 1.7%, respectively.

A solution of the complex (675 mg) and cc-1,5-COD in methanol (180 mL) was purged under nitrogen and irradiated as above for 30 min. After being stirred for 30 min, the photolysate was quickly filtered and washed with cold methanol (2 × 5 mL) to give a solid (593 mg, 88%): UV, see Figure 3c; IR, showed all major peaks of $[CuCl(ct\text{-}1,5\text{-}COD)]_2$ between 1250 and 650 cm^{-1} (Figure 4b). This solid was decomposed as above and the ether extract was analyzed by GC to give ct-1,5-COD (76%) and cc-1,5-COD (23%).

Pyrex Filter. A methanol suspension containing $[CuCl(cc\text{-}1,5\text{-}COD)]_2$ (414 mg, 2 mmol) and cc-1,5-COD (4 mmol) was photolyzed through a Pyrex filter under nitrogen. In 5 min, white precipitates were formed and increased considerably. The solution samples at intervals were treated as above and analyzed by GC to give no peaks other than cc-1,5-COD up to 4 h of irradiation. The white solid was filtered and washed with cold methanol; the solid was treated with concentrated ammonium hydroxide and sodium cyanide and was extracted with ether as above. GC analysis of the ether solution gave peaks at 4.18 (ct-1,5-COD, 28%) and 5.28 min (cc-1,5-COD, 70%). While three minor peaks (≈1%) were also observed, they did not correspond to TCO or tt-1,5-COD.

Preparation of the $[CuCl\text{-}ct\text{-}1,5\text{-}COD]_2$ Complex. $CuCl_2$ (3 g), an ether solution of ct-1,5-COD, and methanol (25 mL) were treated with SO_2 at 0 °C. The solid was filtered and washed with cold methanol to give a white powder of $[CuCl(ct\text{-}1,5\text{-}COD)]_2$ (524 mg): UV and IR spectra, see Figures 3b and 4c; NMR ($CDCl_3$) 2.12 (br m, 8 H), 5.79 (br m, 4 H) ppm; MS (EI), *m/e* (%) 54 (100), 67 (54), 79 (48), 259 (10), 261 (15), 263 (12), 265 (5), 294 (12), 296 (10), 298 (20), 300 (12), 394 (5), 396 (7), 398 (5), 400 (2). The solid (20 mg) was decomposed with NH_4OH and NaCN as before and extracted with ether. GC of the ether solution showed the peaks of ct-1,5-COD (96%) and two unknown peaks at 1.76 (<3%) and 2.11 min (≈1%). The dried sample gave the following elemental analysis: sample 1, C, 26.25; H, 3.27; C/H, 8.03; sample 2, C, 33.43; H, 4.17; C/H, 8.02 (calcd for $CuClC_8H_{12}$, C, 46.38; H, 5.80; C/H 8.00).

Photolysis of $[CuCl(ct\text{-}1,5\text{-}COD)]_2$ in Methanol. The complex (40 mg) in methanol (25 mL) was photolyzed through a Corex filter under nitrogen, and the total mixtures were analyzed at intervals as described above. The results are shown in Figure 6; tt-1,5-COD was not detected in 90 min of irradiation.

A similar suspension was photolyzed through a Pyrex filter and analyzed as above. The percentage of ct-1,5-COD decreased and that of cc-1,5-COD increased to 60:40 in 2 h, but no TCO was formed.

Acknowledgment. We gratefully acknowledge the generous financial support of the work provided by the Natural Science and Engineering Council of Canada.

Registry No. $[CuCl(cc\text{-}1,5\text{-}COD)]_2$, 89015-37-2; CC-1,5-COD, 1552-12-1; ct-1,5-COD, 5259-71-2; tt-1,5-COD, 17612-50-9; $[CuCl(ct\text{-}1,5\text{-}COD)]_2$, 89015-38-3; $Cu(acac)_2$, 46369-53-3; acack, 19393-11-4; Ph_2CO, 119-61-9; $Cu(hfac)_2$, 14781-45-4; cc-1,5-COD–Ph_2CO oxetane, 88947-01-7; $Cu(acac)(PPh_3)_2$, 25427-02-5; Cu(acac)(cc-1,5-COD), 88947-02-8.

Methyl Transfer to Nucleophilic Metal Carbonylate Anions in Catalytic Methanol Homologation

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Received December 2, 1983

The kinetics of the stoichiometric reaction of methyltrialkylammonium cations with nucleophilic metal carbonylate anions was investigated in terms of its relationship to a new catalytic methanol homologation method. At high temperatures and pressures of H_2 and CO, a methyl group from each cation is incorporated into methane or ethanol. In the ionizing solvent, *N*-methylpyrrolidinone, the reaction using iron tetracarbonyl hydride anion is first order in both the methylammonium cation and iron carbonylate anion concentrations and zero order with respect to the partial pressures of hydrogen or carbon monoxide. The enthalpy and entropy of activation, in the temperature range of 180–210 °C, are 44 kcal/mol and +17 eu, respectively. The second-order rate constants exhibit a primary kinetic salt effect, increasing with decreasing salt concentration. The rate constants also increased with decreasing dielectric constant of the solvent. The data are consistent with methyl group transfers (S_N2) between ions as the rate-limiting step. At 200 °C and 245 atm (3:1 CO/H_2) the second-order rate constants, $2.0 \times 10^{-4}\ M^{-1}\ s^{-1}$ for $HFe(CO)_4^-$, $5.3 \times 10^{-4}\ M^{-1}\ s^{-1}$ for $Mn(CO)_5^-$, are a measure of the nucleophilicities of these carbonylates toward tetramethylammonium ion. In the case of the manganate system, the product selectivity (ethanol vs. methane) was found to be independent of H_2 or CO partial pressure between 61 and 184 atm but slightly dependent on the concentration of $Mn(CO)_5^-$. These factors are discussed in terms of reaction mechanism.

Introduction

The homologation of alcohols using cobalt carbonyls was first reported by Wender et al.[2a] in the late 1940s although an earlier (1941) patent using a CoO/NiO catalyst exists.[2b] At 180 °C and 200 atm of synthesis gas (1:1 CO/H_2), the homogeneous catalyst, $HCo(CO)_4$, was observed to ho-

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[1] Graduate Research Participant at Argonne National Laboratory, 1979–1982.

[2] (a) Wender, I.; Friedel, R. A.; Orchin, M. *J. Am. Chem. Soc.* **1949**, *71*, 4160. (b) Weitzel, G.; Eder, K.; Scheuermann, A. (BASF), DE-DS 867 849, 1949.

0276-7333/84/2303-0708$01.50/0