Photochemistry of Cu–Olefin Complexes: a Flash Photochemical Investigation of the Reactivity of Cu(ethylene)$^+$ and Cu(*cis,cis*-1,5-cyclooctadiene)$_2^+$

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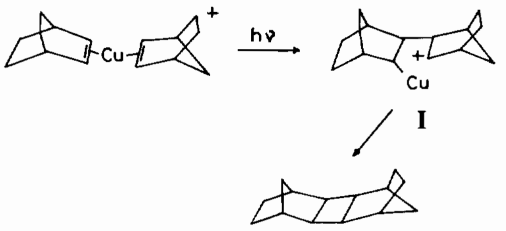
Abstract

The UV-photochemistries of Cu(ethylene)$^+$, Cu$(C_2H_4)^+$, and Cu(*cis,cis*-1,5-cyclooctadiene)$_2^+$, Cu(*c,c*-COD)$_2^+$, have been investigated by continuous and flash photolysis. Photolyses of Cu$(C_2H_4)^+$ in ethylene saturated methanol produce hexane and formaldehyde. This process and the photoinduced photoisomerization of Cu(*c,c*-COD)$_2^+$ to Cu(*c,c*-COD)(*c,t*-COD)$^+$, *c,t*-COD = *cis,trans*-1,5-cyclooctadiene, proceed through several intermediates with lifetimes in a nanosecond–second time domain and spectra with absorption bands in the 400–600 nm range. These intermediates have been assigned as σ-bound copper–alkyl species. The mechanisms for product formation are discussed.

Introduction

The photochemistry of a number of metal–olefin complexes has received some attention in recent years because of its potential applications in photocatalysis and in the conversion and storage of solar energy [1–4]. These studies have demonstrated that the photoproducts are associated with the irradiation of copper-olefin complexes and not with the photolysis of the free olefin [2, 5]. A number of mechanisms have been proposed in order to explain the photoinduced dimerization and valence isomerization of olefins. In some photoprocesses, it has been proposed that the mechanism requires the formation of cationic intermediates, (I), such as in the [CuOTf]-photoassisted dimerization of norbornene, eqn. (1) [6]. Also, the phototransformations of Cu–olefins have been related to the reactivity of intermediates with a delocalized π-system, (II), as in the case of the CuCl-photoassisted isomerization of norbornadiene to quadricyclane, eqn. (2) [7]. In the related photoisomerization of olefins induced by carbonyl complexes it has been assumed that a σ-bound diradical, (III) in eqn. (3), is a reaction intermediate [8–9]. The formation of intermediates with a diradical nature has not been investigated in the photochemistry of Cu–olefin complexes.



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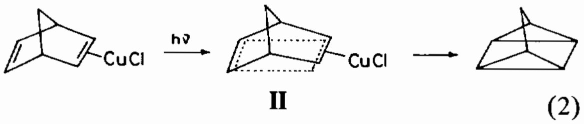

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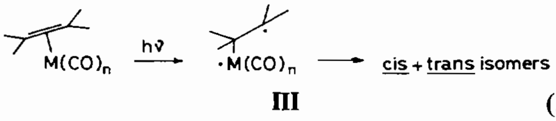

(3)

The proposition of intermediates in these mechanisms has been based on the nature of the reaction products and the effect of scavengers on the reaction course. Therefore, it is interesting from a mechanistic stand point to investigate the photochemistry of the copper–olefins with techniques, *i.e.* flash photolysis, that allow the direct observation of such intermediates. Two complexes that exhibit thermal properties appropriate for these studies are Cu$(C_2H_4)^+$ and Cu(*c,c*-COD)$_2^+$†. Moreover, Whitesides *et al.* [4], and Kutal *et al.* [2], have demonstrated that, in the photochemistry of Cu(*c,c*-COD)$_2^+$, the primary reaction is the formation of Cu(*c,c*-COD)(*c,t*-COD)$^+$, eqn. (4).

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†Abbreviations: *c,c*-COD, *cis,cis*-1,5-cyclooctadiene; *c,t*-COD, *cis,trans*-1,5-cyclooctadiene, OTf, trifluoromethanesulfonate.

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$$Cu(c,c\text{-}COD)_2^+ \xrightarrow{h\nu} Cu(c,c\text{-}COD)(c,t\text{-}COD)^+ \quad (4)$$

In this context, we have studied the photoreactivity of these model systems, *i.e.* $Cu(C_2H_4)^+$ and $Cu(c,c\text{-}COD)_2^+$, in order to obtain information on reaction mechanisms which potentially involve diradical intermediates.

Experimental

Photochemical Procedures

A low pressure Hg spectral lamp was used for continuous photolysis at 254 nm.

Flash photochemical experiments were carried out with apparatuses described elsewhere [10]. For spectral determinations or the study of reaction kinetics that required observations at times longer than 30 μs, the photolyte was irradiated with two xenon flash lamps fired in series at various energies (40 to 250 J/pulse). Excitations with a Nd yag, λ_{excit} = 266 nm, in laser flash photolysis were used for experiments in a nanosecond time domain. The data were processed in a Varian PDP 11/55 computer system. In the computer analyses of the data associated with absorption changes, each point for the spectrum was obtained from an average of 5 to 10 experiments. Rate constants were obtained from least squares treatments; a hundred data points derived from an average of 5 to 10 traces were used in the treatments.

Analytical Procedures

The concentration of copper(II) species was determined by the 2,9-dimethyl-1,10-phenanthroline ascorbic acid procedure [11]. Formaldehyde was investigated by a procedure reported elsewhere [12]. Hydrocarbons such as hexane were analyzed by GC and/or MS after separation from the copper species. For this separation, 0.1 M KCN was added to irradiated solutions and blanks in order to obtain solutions with a cyanide to copper molar ratio larger than 2:1. The condensable products and the solvent were distilled from the solid salts in a vacuum line and samples of the distillated were used for the analysis of the products. In some experiments, the vacuum distillation was replaced by the extraction of the products from the methanolic solution with nonane.

Materials

Copper(I) complexes, $Cu(C_2H_4)^+$ and $Cu(c,c\text{-}COD)_2^+$, were prepared according to reported procedures [13, 14]. The complex $Cu(C_2H_4)^+$ was prepared *in situ*. A solution of $Cu(OTf)_2$ in ethylene saturated methanol and a large excess of copper powder were vigorously agitated with streams of C_2H_4 for several hours. The blue color of the Cu(II) ions faded as the reduction took place. The solution was filtered to remove excess Cu(0) and aliquots of the solution were removed with a gas tight syringe. The complex is extremely air sensitive and all the manipulations had to be performed under an ethylene atmosphere. In methanolic solutions the spectrum of the complex exhibited bands at 276 nm (990 M^{-1} cm^{-1}) and 220 nm (3950 M^{-1} cm^{-1}).

The $Cu(c,c\text{-}COD)_2OTf$ was prepared by reduction of $Cu(OTf)_2$ with copper powder. For this preparation 13.0 g (0.0359 mol) of $Cu(OTf)_2$, 4.6 g (0.0719 mol) of Cu powder and 31.1 g (0.288 mol) of *cis,cis*-1,5-cyclooctadiene along with 50 cm^3 of methanol were stirred together with streams of Ar. The blue solution turned green and the color faded at longer times. The liquid was separated from the excess metallic copper by filtration and partly evaporated under vacuum in order to precipitate the complex. The white solid was dried under vacuum at room temperature. Yield: 45%. The IR of the compound and elemental analysis were in agreement with reports in the literature. Calculated: %C = 47.60 and %H = 5.64. Found: %C = 47.58 and %H = 5.66, was that expected for $Cu(c,c\text{-}COD)_2OTf$.

Other materials were analytical grade and used without further purification.

Results

Continuous Photolysis

The 254 nm photolyses of $Cu(C_2H_4)^+$ in ethylene-saturated methanol produce hexane and formaldehyde. In experiments where the concentration of ethylene remained constant throughout the photolysis, the spectra of solutions irradiated for variable periods exhibit no differences with the spectrum of $Cu(C_2H_4)^+$ in unphotolyzed blanks. Nonetheless, the bleach of the $Cu(C_2H_4)^+$ absorption bands, Fig. 1, have been observed when the photochemical reaction causes the depletion of C_2H_4. Such a depletion of ethylene eventually leads to the formation of metallic copper through the disproportionation of cuprous ions. In photolyses carried out with a constant ethylene concentration, the yield of formaldehyde depends on the ethylene concentration, namely $\phi \sim 5.4 \times 10^{-3}$ for $[C_2H_4] \sim 0.10$ M and $\phi \sim 2.8 \times 10^{-3}$ for $[C_2H_4] \sim 0.045$ M.

The progress of the 254 nm photolyses of $Cu(c,c\text{-}COD)_2^+$ in methanol was followed by means of the NMR and UV-spectra. Absorption spectra recorded at various irradiation times reveal the formation of new maxima, Fig. 1, at λ_{max} = 235, 290 nm. This and the NMR analyses of the photolyzed solutions are in agreement with the reported formation of $Cu(c,c\text{-}COD)(c,t\text{-}COD)^+$ as an initial reaction

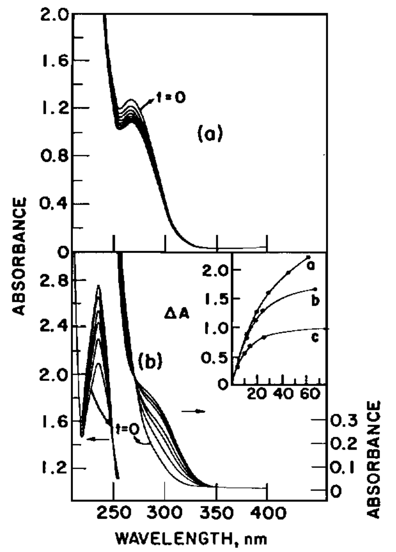


Fig. 1. Spectral changes determined at 3 min intervals in 254 nm continuous photolyses for (a) Ar-saturated solutions of $Cu(C_2H_4)^+$ and (b) Ar-saturated solutions of $Cu(c,c\text{-}COD)_2^+$ in methanol. The insert to (b) shows the change in the optical density, ΔA, at 290 nm with irradiation time for $[Cu(c,c\text{-}COD)_2^+]$ = (a) $2 \cdot 10^{-2}$ M, (b) $5 \cdot 10^{-3}$ M and (c) 10^{-3} M.

product. That in extended photolyses this product enters in secondary photochemical transformations, *i.e.* leading to the reorganization of the ligand into products such as tricyclo$[3,3,0,0^{2,6}]$octane, is evident from the non linear dependence of the $Cu(c,c\text{-}COD)(c,t\text{-}COD)^+$ concentration on the irradiation time, insert to Fig. 1. Indeed, the growth of the absorbance at either 235 or 290 nm varies in a non linear manner with irradiation time, and the departures from linearity diminish with increasing concentrations of $Cu(c,c\text{-}COD)_2^+$. Similar evidence with regard to the secondary photolysis of $Cu(c,c\text{-}COD)(c,t\text{-}COD)^+$ has been obtained by following the transformations of the NMR spectrum as a function of the length of the irradiation. Copper(II) complexes and formaldehyde have not been detected in concentrations above the detection limit of our procedures, *e.g.* $\sim 10^{-7}$ M, in experiments with a negligible secondary photolysis of $Cu(c,c\text{-}COD)(c,t\text{-}COD)^+$. The 254 nm photolysis of $Cu(c,c\text{-}COD)_2^+$ in THF yield the same results of the photolysis in methanolic solutions, and (in either THF or methanol) the photochemistry is independent of the concentration of added electrolytes, *e.g.* 0.1 M ⩾ $[NaClO_4]$ or 0.1 M ⩾ [NaOTf].

Flash Photolysis

Flash photolysis of $Cu(C_2H_4)^+$ in ethylene-saturated methanol reveals that several intermediates are involved in the formation of the stable products. Indeed, the spectrum of the flash irradiated solution experiences transformations which correspond to three different steps in the reaction, Fig. 2. In a first step, a species that absorbs at λ_{max} = 320 nm is formed in a time shorter than 15 ns, *i.e.* the time resolution of our apparatus, and evolves into a species with λ_{max} = 500 nm. This process obeys a first order rate law with a rate constant, $k = (2.1 \pm 0.3) \times 10^6\ s^{-1}$. The product of the first step (λ_{max} = 500 nm in Fig. 2) transforms into a long-lived intermediate (λ_{max} = 360 nm) in a second step. The rate of such a transformation exhibits a first order dependence on the concentration of the intermediate with λ_{max} = 500 nm. The third step, namely the decay of the 360 nm transient, regenerates the $CuC_2H_4^+$ spectrum. Such a process obeys a first order rate law with a rate constant, $k = (78 \pm 5)\ s^{-1}$.

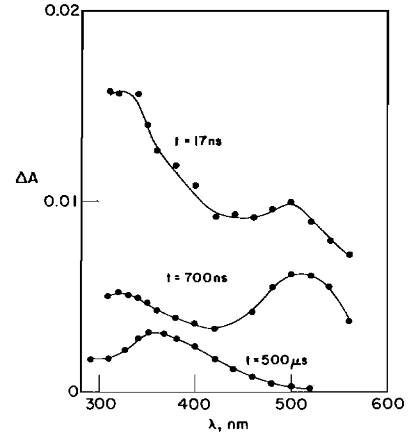


Fig. 2. Difference spectra at three instants of the reaction induced in flash irradiations of $Cu(C_2H_4)^+$ in ethylene-saturated methanolic solutions.

Two precursors of $Cu(c,c\text{-}COD)(c,t\text{-}COD)^+$ have been observed in flash irradiations of $Cu(c,c\text{-}COD)_2^+$ in methanol. The first transient, λ_{max} = 290 nm, undergoes a transformation into a second transient by a first order process with $k = (7.3 \pm 0.4) \times 10^5\ s^{-1}$, Fig. 3. The second intermediate, λ_{max} = 320 nm, converts to $Cu(c,c\text{-}COD)(c,c\text{-}COD)^+$ via a first order process, $k = (2.9 \pm 0.3) \times 10^{-1}\ s^{-1}$, independent of ionic strength, $10^{-3}\ M \leqslant [NaClO_4] \leqslant 0.1$ M, and c,c-COD, $10^{-4}\ M \leqslant [c,c\text{-}COD] \leqslant 0.1$ M. The same transients have been observed in flash irradiations of $Cu(c,c\text{-}COD)_2^+$ in THF.

Discussion

The photoprocess induced in UV-irradiations of $Cu(C_2H_4)^+$ in ethylene–methanol mixtures can be described as a reductive polymerization of ethylene which takes place at expenses of the oxidation of the solvent. In this context, the results

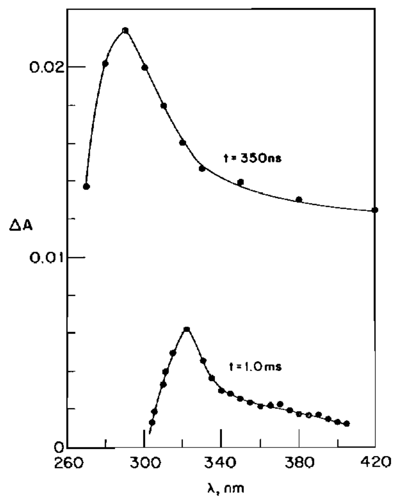
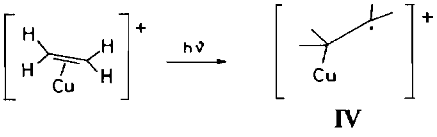


Fig. 3. Difference spectra of the two intermediates observed in flash irradiations of $Cu(c,c\text{-}COD)_2^+$ in methanol.

suggest that the formation of the products in photolyses of $Cu(C_2H_4)^+$ is largely determined by the production of radical-like species which can be rapidly intercepted by ethylene[‡]. The spectral transformations observed in flash photolysis of $Cu(C_2H_4)^+$ exhibit the features that are characteristic of intermediates with copper–alkyl bonds[†]. Moreover, the formation of an intermediate with this nature at times shorter than or equal to 15 ns signals that such species must be produced shortly after the primary process. It is possible to relate these observations with a proposition that adscribes the photoreactivity of some olefinic complexes to the formation of 'diradical species', namely species containing two unpaired electrons at a remote carbon and at the metal center respectively [8, 9]. Similar diradicals, *i.e.* the species (**IV**) in eqn. (5), might lead to the formation of the first observed intermediate (the species with λ_{max} 320 nm in Fig. 2) by reaction with ethylene, eqn. (5)–(7). The disappearance of the diradical, eqns. (6), (7), is expected to be extremely fast, *i.e.* these processes must be over in less than 10 ns. In this context, we propose that (in flash photolysis) the spectral transformations corresponding to the first step are related to the equilibration between the first observed species and a bidentate copper–alkyl derivative which has an absorption band with λ_{max} = 500 nm, Fig. 2 and eqn. (8)[≠].



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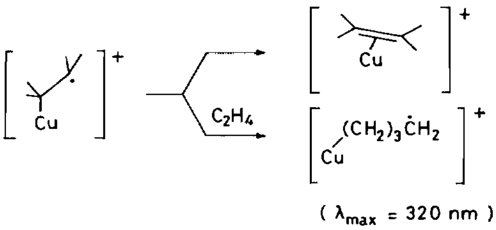

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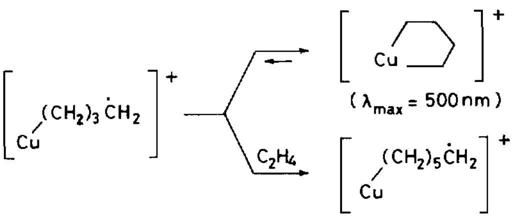
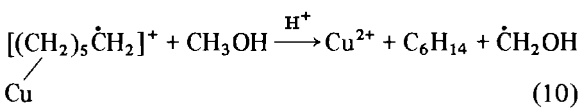


(8)

(9)

Furthermore, the formation of stable products (formaldehyde and hexane) and the transients observed in flash photolysis suggest that the intermediate is scavenged by ethylene, eqn. (9), and that reactions with the solvent, eqn. (10), or with solvent radicals, eqn. (11)–(14), lead to the catalytic recycling of copper(I) as it is described in eqns. (10)–(14).



$$[\underset{Cu}{(CH_2)_5\dot{C}H_2}]^+ + CH_3OH \xrightarrow{H^+} Cu^{2+} + C_6H_{14} + \dot{C}H_2OH \qquad (10)$$

$$Cu^{2+} + \dot{C}H_2OH \longrightarrow Cu^+ + CH_2O + H^+ \qquad (11)$$

$$\begin{tikzcd} & (CH_2OH)_2 \quad (12) \\ 2\dot{C}H_2OH \arrow[ur] \arrow[dr] & \\ & CH_2O + CH_3OH \quad (13) \end{tikzcd}$$

$$Cu^+ + C_2H_4 \rightleftharpoons Cu(C_2H_4)^+ \qquad (14)$$

In the photochemistry of $Cu(c,c\text{-}COD)_2^+$, the absence of redox reactions involving the solvent stands in contrast with the oxidation of methanol in photolyses of $Cu(C_2H_4)^+$. Therefore, if diradical-like intermediates are photogenerated with $Cu(c,c\text{-}COD)_2^+$, they must be poor oxidants and/or shorter lived than the homologous species produced with $Cu(C_2H_4)^+$. The observation of intermediates in flash photolysis is in agreement with this proposition,

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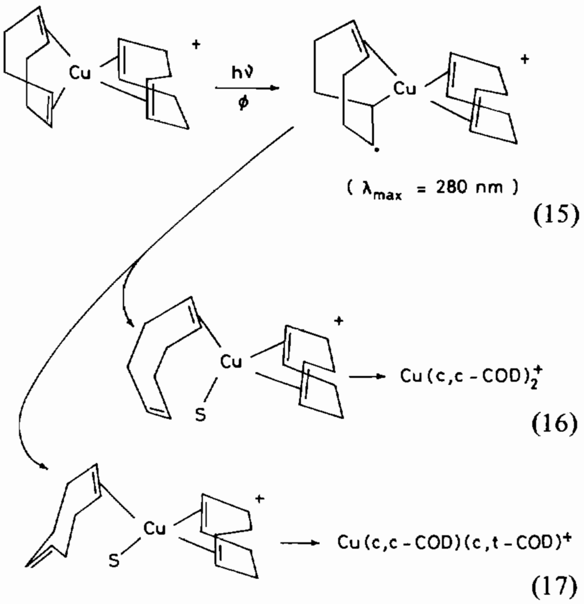
[‡] It must be pointed out that the independence of the photochemical transformations on solvent (methanol, THF) and ionic strength is incompatible with mechanistic models based on the formation of reactive carbon-cations.

[†] For a review on copper–alkyl species see ref. [15].

[≠] The transient cuprocyclopentane has the reactivity of other metallocyclopentanes, namely as intermediates of [2 + 2] cycloaddition of olefins [16, 17].

and the experimental results can be interpreted in terms of a mechanism which involves two metastable alkyl–copper species, eqn. (15)–(17), in the formation of Cu(*c*,*c*-COD)(*c*,*t*-COD)$^+$



The formation of transient species with diradical nature in photolyses of Cu$(C_2H_4)^+$ and Cu(*c*,*c*-COD)$_2^+$ can be seen as a manifestation of structural impedements to the formation of intermediates with a delocalized π-system such as the one proposed for the copper(I)-photoinduced valence isomerization or norbornadiene.

Acknowledgements

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