Journal of Organometallic Chemistry, 332 (1987) 229–238
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Complex formation during the cyclization of 1-diazo-3-phenoxy-2-propanone catalyzed by bis(hexafluoroacetoacetonato)copper(II)

Mario Branca, Giovanni Micera and Antonio Saba*
Dipartimento di Chimica, Universita' di Sassari, Via Vienna 2, 07100 Sassari (Italy)

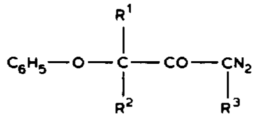
(Received January 23rd, 1987)

Abstract

The cyclization of 1-diazo-3-phenoxypropanone to give 3-oxo-3,4-dihydro-2*H*-1-benzopyran, catalyzed by $[Cu(Hfac)_2]$ or $[Cu(Hfac)_2(H_2O)_2]$, Hfac = hexafluoroacetoacetonato, has been studied in toluene and dichloromethane solution by spectroscopic methods (ESR, NMR, and electronic absorption). The results show that the substrate initially coordinates to the copper atom through the carbonyl group yielding mono- and bis-adducts. At high substrate/catalyst ratios the copper atom undergoes reduction and soluble ESR-inactive species, probably involving copper(I), are formed together with copper(0) colloidal precipitates. At the same time ESR signals due to organic radicals are observed. With decreasing substrate/catalyst ratios, an increasing proportion of the copper remains in the copper(II) oxidation state and, in this case coordination of the catalyst to the reaction product is also observed.

Introduction

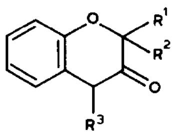
α′-Aryloxy-α-diazo ketones I are cyclized to 3-chromanones II and cycloheptatriene-3-furanones III under catalysis by $[Cu(Hfac)_2]$ under mild conditions in CH_2Cl_2 solution [1]. Such cyclizations are thought to proceed by intramolecular addition of an initially formed ketocarbenoid species to the activated *ortho* position of the phenoxy group "via" a norcaradienic intermediate (IV) [2].



$$C_6H_5{-}O{-}\underset{R^2}{\overset{R^1}{C}}{-}CO{-}\underset{R^3}{C}N_2$$

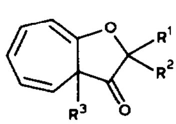
(I)

Ia: $R^1 = R^2 = R^3 = H$

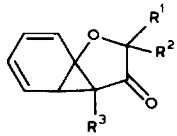


(II)

IIa: $R^1 = R^2 = R^3 = H$



(III)



(IV)

0022-328X/87/$03.50

Alternatively, the 3-chromanones II may originate from a Friedel–Crafts type attack of the metal-ketocarbenoid, with its partial cationic character [3], to the aromatic ring. This explanation implies the presence of a carbene-copper complex in which the carbene moiety is bonded transiently to the metal as a fifth ligand [4].

Stable carbene complexes of a variety of metals are known, but none of copper, probably owing to the high reactivity of these species [5]. Thus, to find out whether in such reactions copper interacts with the substrate and eventually undergoes a change of its oxidation state, we investigated the $[Cu(Hfac)_2]$/1-diazo-3-phenoxy-2-propanone Ia system by spectroscopic methods (ESR, NMR and electronic absorption) before, during, and at the end of the cyclization. The catalyst was used in either hydrated, $[Cu(Hfac)_2(H_2O)_2]$, or anhydrous, $[Cu(Hfac)_2]$, form. The reaction was carried out in toluene or dichloromethane.

Results and discussion

Reaction in toluene

Dissolution of $[Cu(Hfac)_2]$ or $[Cu(Hfac)_2(H_2O)_2]$ in toluene under our conditions yielded glassy ESR spectra (Fig. 1a) similar each to other and with spin-Hamiltonian parameters ($g_{\parallel} = 2.282$, $A_{\parallel} = 178 \times 10^{-4}$ cm^{-1}) identical to those reported by Yokoi [6] for planar $[Cu(Hfac)_2]$ molecules (V), see Table 1, in the same solvent. The electronic spectra (Fig. 2) were also consistent with that described by Yokoi.

Addition of substrate, at 5 °C to avoid reaction, resulted in a red shift of the *d–d* absorption bands, indicating adduct formation between $[Cu(Hfac)_2]$ and the substrate, and in the appearance of well-resolved ESR signals (Fig. 1b) attributable to two tetragonal complex species. On the basis of the known relationships between axiality and ESR parameters for tetragonal copper(II) complexes, it can be inferred that the species yielding the lower $g_{\parallel}$ value and the higher parallel hyperfine coupling constant ($g_{\parallel} = 2.329$ and $A_{\parallel} = 155 \times 10^{-4}$ cm^{-1}) is the mono-adduct VI, while that with $g_{\parallel} = 2.346$ and $A_{\parallel} = 146 \times 10^{-4}$ cm^{-1}) is the bis-adduct VII. The relative intensities of the ESR signals varied as a function of the substrate/copper(II) complex molar ratio, in accord with expectation for equilibria involving formation of adducts.

When the substrate was allowed to react, the ESR signals become progressively weaker, those of the bis-adduct more rapidly than those of the mono-adduct (Fig. 1c). Finally, a broad featureless resonance was observed, which disappeared as a radical signal at *g* ca. 2 showed up (Fig. 3). However, when a substrate/catalyst molar ratio as low as 15 was employed, the reaction was much faster and paramagnetic copper(II) species were detected by ESR spectroscopy whatever the extent of reaction. Thus as reaction took place, a new copper(II) species VIII appeared (Fig. 1d) and was the only ESR detectable copper(II) complex in the final stage (Fig. 1e). The radical signal was again observed.

To identify species VIII, the interaction of $[Cu(Hfac)_2]$ with 3-oxo-3,4-dihydro-2*H*-1-benzopyran IIa, the main product [1], was investigated in toluene by ESR spectroscopy. By varying the molar ratio of chromanone to $[Cu(Hfac)_2]$ the stepwise formation of two complex species IX and X could be observed (Figs. 1f and 1g). Species IX, with $g_{\parallel} = 2.339$ and $A_{\parallel} = 153 \times 10^{-4}$ cm^{-1}, which was formed at the highest substrate/$[Cu(Hfac)_2]$ molar ratios, can be identified as the bis-adduct. The decrease of the chromanone/$[Cu(Hfac)_2]$ ratio shifted the equilibrium toward the

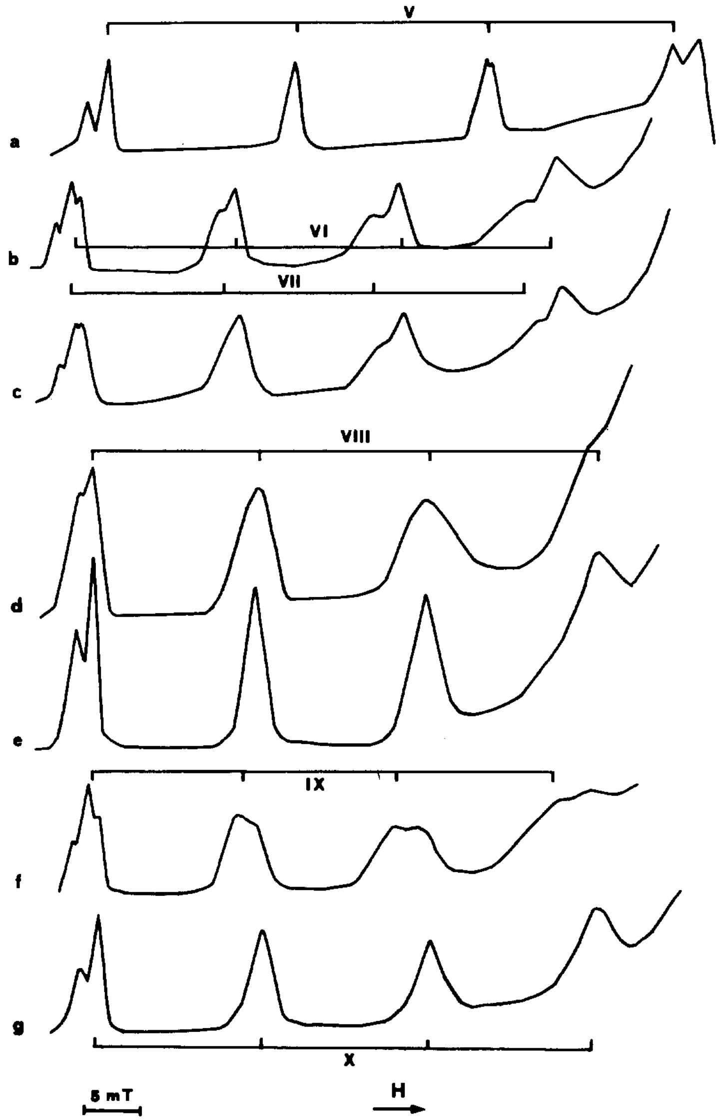
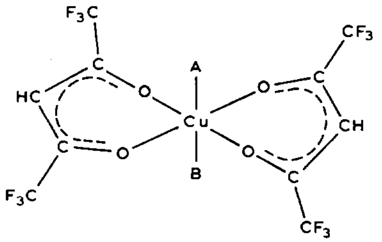


Fig. 1. X-Band ESR spectra (g-parallel region) recorded at 120 K for toluene solutions: [Cu(Hfac)$_2$] or [Cu(Hfac)$_2$(H$_2$O)$_2$] 5.5×10^{-4} *M* (a), [Cu(Hfac)$_2$] 5.5×10^{-4} *M* after addition of substrate 1.65×10^{-1} *M* at 5°C (b), [Cu(Hfac)$_2$] 5.5×10^{-4} *M* plus substrate 1.65×10^{-1} *M* after reaction at room temperature for half a minute (c), [Cu(Hfac)$_2$] 5.5×10^{-3} *M* plus substrate 8.25×10^{-2} *M* after reaction at room temperature for half a minute (d) and for 4 h (e), [Cu(Hfac)$_2$] 5.5×10^{-3} *M* plus chromanone 5.5×10^{-1} *M* (f), and [Cu(Hfac)$_2$] 5.5×10^{-3} *M* plus chromanone 6.6×10^{-2} *M*.

monoadduct X ($g_{\parallel} = 2.315$ and $A_{\parallel} = 159 \times 10^{-4}$ cm^{-1}), where the metal coordination becomes more tetragonally distorted. Species X exhibits the same spectral parameters as VIII, which is thus identified as the mono-adduct of [Cu(Hfac)$_2$] with chromanone.

Table 1

Proposed structures for the species V–XVII [a]



Catalyst	Solvent	Species	A	B
$[Cu(Hfac)_2]$ or $[Cu(Hfac)_2(H_2O)_2]$	Toluene	V	–	–
$[Cu(Hfac)_2]$ or $[Cu(Hfac)_2(H_2O)_2]$	Toluene	VI	substrate	–
$[Cu(Hfac)_2]$ or $[Cu(Hfac)_2(H_2O)_2]$	Toluene	VII	substrate	substrate
$[Cu(Hfac)_2]$ or $[Cu(Hfac)_2(H_2O)_2]$	Toluene	VIII [b], X [c]	chromanone	–
$[Cu(Hfac)_2]$ or $[Cu(Hfac)_2(H_2O)_2]$	Toluene	IX	chromanone	chromanone
$[Cu(Hfac)_2]$	CH_2Cl_2	XI	substrate	–
$[Cu(Hfac)_2]$	CH_2Cl_2	XII	chromanone	–
$[Cu(Hfac)_2(H_2O)_2]$	CH_2Cl_2	XIII	water	water
$[Cu(Hfac)_2(H_2O)_2]$	CH_2Cl_2	XIV	substrate	water
$[Cu(Hfac)_2(H_2O)_2]$	CH_2Cl_2	XV	chromanone	–
$[Cu(Hfac)_2(H_2O)_2]$	CH_2Cl_2	XVI [b], XVII [c]	chromanone	water

[a] The spectral results indicate that the substrate and the reaction product, chromanone, coordinate to copper(II) through the oxygen atom of the carbonyl group. [b] Species detected during reaction. [c] Species detected in the binary interaction of catalyst with chromanone.

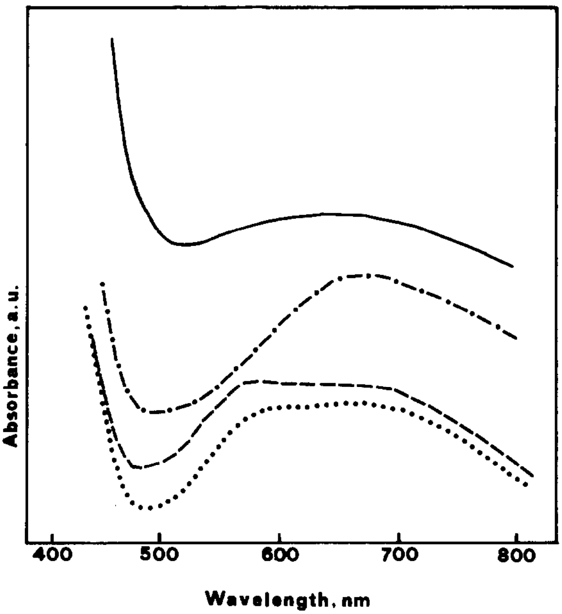


Fig. 2. Electronic spectra recorded at 5 °C for toluene solutions: $[Cu(Hfac)_2(H_2O)_2]$ 5.5×10^{-3} *M* (······), $[Cu(Hfac)_2]$ 5.5×10^{-3} *M* (— — —), $[Cu(Hfac)_2]$ 5.5×10^{-3} *M* plus substrate 8.25×10^{-2} *M* immediately after mixing (·–·–·) and after reaction for 4 h (———).

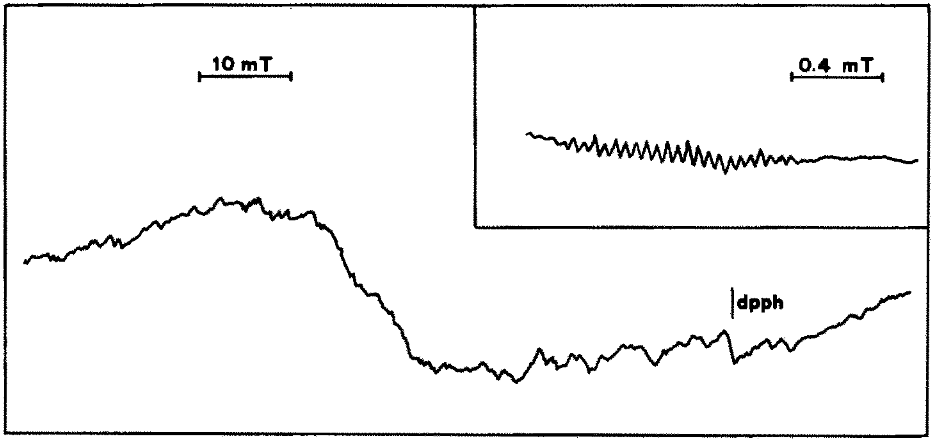


Fig. 3. X-Band ESR spectrum recorded at 120 K for a toluene solution of $[Cu(Hfac)_2]$ 5.5×10^{-4} *M* plus substrate 1.65×10^{-1} *M* after reaction for a minute at room temperature. The insert shows the ESR signals (recorded at room temperature) of the radical species.

Reaction in dichloromethane

Whatever the concentration of the solution anhydrous $[Cu(Hfac)_2]$ was found not to yield magnetically dilute species (i.e. without interaction between paramagnetic copper centres) in CH_2Cl_2, as judged from the ESR spectra. Addition of the substrate allowed observation of well-resolved ESR spectra (Fig. 4a), supporting the formation of a main species XI, which on the basis of its spectral parameters

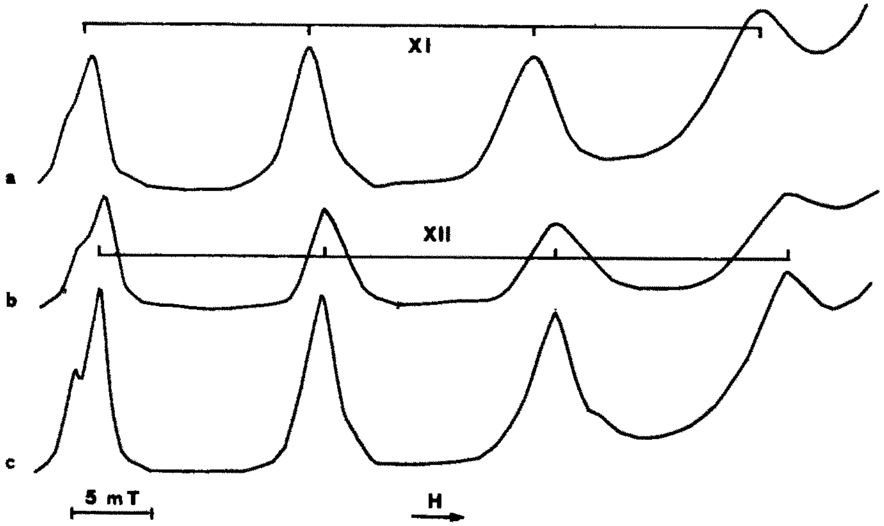


Fig. 4. X-Band ESR spectra (*g*-parallel region) recorded at 120 K for dichloromethane solutions: $[Cu(Hfac)_2]$ 1.1×10^{-3} *M* after addition of substrate 5.5×10^{-2} *M* at 5 °C (a), $[Cu(Hfac)_2]$ 1.1×10^{-3} *M* plus substrate 5.5×10^{-2} *M* after reaction at room temperature for 2 minutes (b) and $[Cu(Hfac)_2]$ 5.5×10^{-3} *M* plus chromanone 1.6 *M* (c).

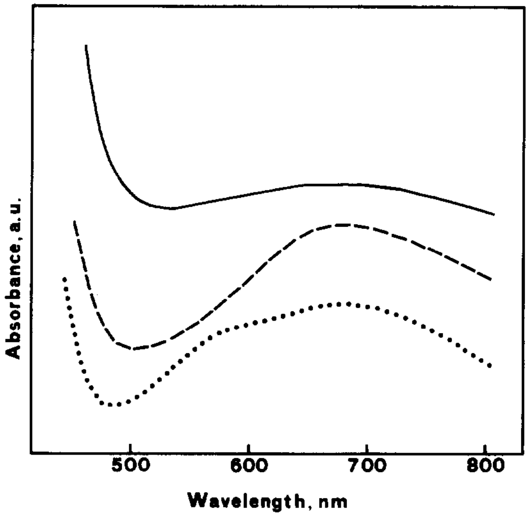


Fig. 5. Electronic spectra recorded at 5 °C for dichloromethane solutions: [Cu(Hfac)$_2$] 1.1×10^{-3} *M* (······), [Cu(Hfac)$_2$] 1.1×10^{-3} *M* plus substrate 5.5×10^{-2} *M* (— — —) immediately after mixing and [Cu(Hfac)$_2$] 1.1×10^{-3} *M* plus substrate 5.5×10^{-2} *M* after reaction at room temperature for 1 h (———).

($g_{\parallel} = 2.337$ and $A_{\parallel} = 153\times10^{-4}$ cm^{-1}), was identified as the 1/1 adduct of [Cu(Hfac)$_2$] with the substrate. The coordination of copper(II) to 1-diazo-3-phenoxy-2-propanone was confirmed also by electronic absorption and NMR spectroscopy. In particular, while the *d–d* absorption bands for [Cu(Hfac)$_2$], Fig. 5, are typical of planar copper(II) β-diketonato complexes, the broad absorption centered at about 675 nm, observed upon addition of substrate to the complex solution, indicates a less planar geometry at the copper ion. ^{1}H NMR "inversion recovering" experiments performed on the starting diazo ketone (in CD_2Cl_2 solution, *T* 253 K) gave the following parameters: T_1(CH) 0.4016 s; T_1(CH$_2$) 0.869 s; T_1(CH arom.) 0.578 s; T_2(CH) 0.88 s; T_2(CH$_2$) 0.94 s. These changed, after addition of the copper complex, into: T_1(CH) 8.33 s; T_1(CH$_2$) 11.42 s; T_1(CH arom) 5.34 s; T_2(CH) 4 s and T_2(CH$_2$) 11.11 s. These results favour coordination of substrate to copper via the carbonyl function. In this case, also, the intensity of the ESR spectrum decreased during the reaction, and, finally, only a broad resonance was apparent. Concurrent formation of colloidal copper(0) was observed; this behaviour has been observed in other systems [5].

At high copper(II) concentrations a new complex species XII, Fig. 4b, with $g_{\parallel} = 2.328$ and $A_{\parallel} = 161\times10^{-4}$ cm^{-1}, was formed as the substrate was used up in the reaction. Species XII was identified as a 1/1 adduct formed by chromanone with [Cu(Hfac)$_2$], as confirmed by the ESR examination of the corresponding binary system (Fig. 4c).

When the dihydrate complex [Cu(Hfac)$_2$(H$_2$O)$_2$] was used as the catalyst, different results were obtained. In this case, the ESR spectra obtained from frozen solutions appeared to be resolved even in the absence of substrate. A six-coordinate species, probably involving the water molecules as the axial donors, was indicated by the ESR parameters (XIII: $g_{\parallel} = 2.354$ and $A_{\parallel} = 140\times10^{-4}$ cm^{-1}), Fig. 6a, on

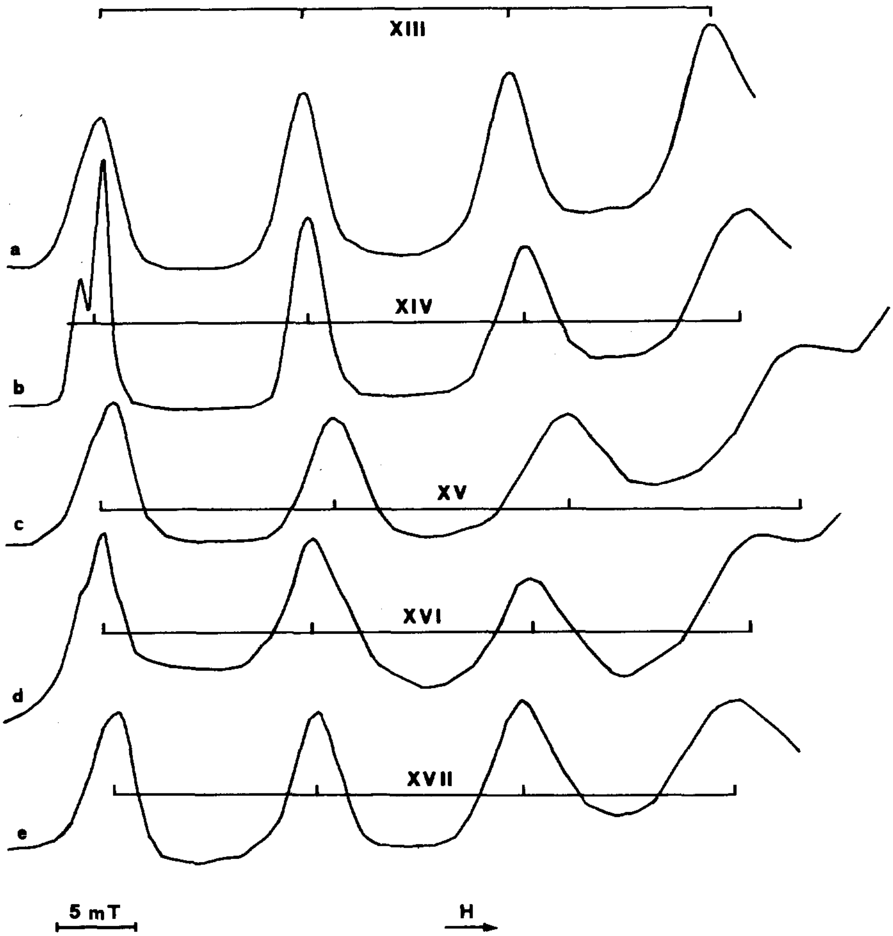


Fig. 6. X-Band ESR spectra (g-parallel region) recorded at 120 K for dichloromethane solutions: $[Cu(Hfac)_2(H_2O)_2]$ 5.5×10^{-4} M (a), $[Cu(Hfac)_2(H_2O)_2]$ 5.5×10^{-4} M after addition of substrate 1.65×10^{-1} M at 5 °C (b), $[Cu(Hfac)_2(H_2O)_2]$ 5.5×10^{-3} M plus substrate 8.25×10^{-2} M after reaction for 2 minutes (c) and after reaction for 2 h (d) and $[Cu(Hfac)_2(H_2O)_2]$ 5.5×10^{-4} M plus chromanone $6.6 \times 10^{-}$ M (e).

the basis of literature data [7], and by the position of the copper(II) *d–d* absorption maximum (Fig. 7). Although slight, the spectral changes produced by addition of substrate confirmed the interaction of the metal center of the catalyst with 1-diazo-3-phenoxy-2-propanone to yield a species (XIV: $g_{\parallel} = 2.349$ and $A_{\parallel} = 149 \times 10^{-4}$ cm^{-1}), Fig. 6b, which has the same overall geometry as the diaqua complex and, decays during the reaction as described before.

Again, only with substantially high copper(II) to substrate ratios was binding of metal to the reaction product observed. In this case after some time two main species were present. The more planar one (XV: $g_{\parallel} = 2.332$ and $A_{\parallel} = 152 \times 10^{-4}$ cm^{-1}), most likely a mono-adduct, was a transient species which predominated only at the end of reaction (Fig. 6c). This was progressively transformed into a six-coordinate complex (XVI: $g_{\parallel} = 2.343$ and $A_{\parallel} = 148 \times 10^{-4}$ cm^{-1}), Fig. 6d, which closely

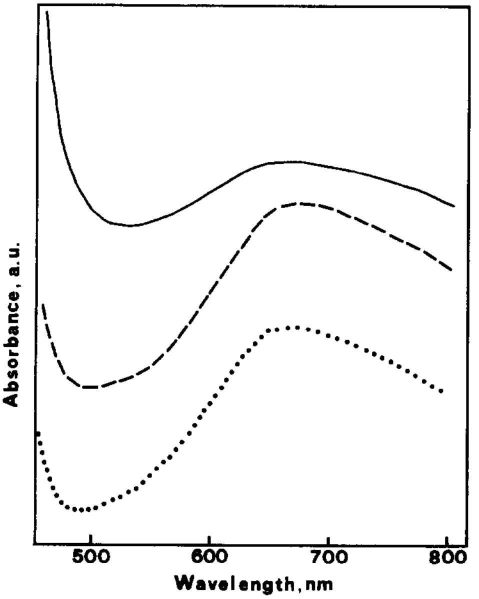


Fig. 7. Electronic spectra recorded at 5 °C for dichloromethane solutions: [Cu(Hfac)$_2$(H$_2$O)$_2$] 5.5×10^{-3} *M* (······), [Cu(Hfac)$_2$(H$_2$O)$_2$] 5.5×10^{-3} *M* plus substrate 8.25×10^{-2} *M* immediately after mixing (— — —) and after reaction for 2 minutes (———).

resembles the main species (XVII: $g_{\parallel} = 2.348$ and $A_{\parallel} = 145 \times 10^{-4}$ cm^{-1}) formed in interaction of chromanone with the catalyst in the same solvent (Fig. 6e).

Overall, in spite of the observed differences, the results obtained with [Cu(Hfac)$_2$] and [Cu(Hfac)$_2$(H$_2$O)$_2$] are generally consistent. It appears that in both cases only one type of adduct is formed by reaction of the catalyst with the substrate. A reasonable explanation is that both these adducts involve a single axial bond between copper and substrate, but that formed by the diaqua complex may retain a water molecule in the sixth position. The same arguments could account for the different structures of the adducts with chromanone (XII and XVI). An apparent exception is XV which, although formed by the diaqua complex, seems to have a five-coordinate (square-pyramidal) structure, and exhibits spectral parameters coincident with those of XII, the "true" mono-adduct with chromanone. In this case, probably complete detachment of water molecules from the copper coordination occurs as a consequence of a rearrangement due to reaction. Subsequently this species further binds water to restore six-coordination, which seems to predominate when the diaqua complex is the catalyst.

Conclusions

The results described reveal that during the cyclization of 1-diazo-3-phenoxypropanone to 3-oxo-3,4-dihydro-2*H*-1-benzopyran in the presence of bis(hexafluoroacetoacetonato)copper(II) as the catalyst, there are common features whatever the reaction condition used. Thus the first reaction step is always the interaction of the substrate with the catalyst to give mono- and bis-adducts. The ESR data, which are typical of copper(II) chromophores involving only oxygen donors, and the NMR data for these adducts confirm that there is coordination of the oxygen atom of the carbonyl group, and that the substrate occupies the axial positions (A, or A and B, in Table 1) at copper through the carbonyl oxygen. Then, as the reaction proceeds, the ESR signals of the adducts diminish, indicating that there is a change in the copper valence state. Magnetic coupling of copper(II) with other paramagnetic centers, which weakens the ESR signals is unlikely, because copper(II) paramagnetic species are no longer detected, even at the end of reaction when only the reaction product coexists with the metal complex. On the other hand, the irreversible change of the copper valence state coincides with the appearance of radical species, further confirming the occurrence of redox reactions. The formation of colloidal copper(0) may be due to secondary reactions or to a disproportionation, as previously suggested [5].

With decreasing substrate/catalyst molar ratios, part of copper(II) retains its valence state and interacts with the reaction product to form adducts in which the oxygen atom of the carbonyl group is in the axial positions (A, or A and B, in Table 1) of the copper coordination sphere.

As to the reaction mechanism, formation of copper carbenoid species is usually assumed to take place during the catalytic decomposition of diazo compounds; even though they have never been observed, their nature and, particularly, the valence state of the copper in them, have long been questioned, and some experimental results favour copper(I) and some copper(II), as the catalytic species [8]. Our results demonstrate that when suitable groups, such as carbonyl groups, having affinity for copper(II) are present in the substrate, "normal" copper(II) complexes may be formed, with the metal ion retaining its valence state. However, reaction drastically alters the magneto-electronic properties of the metal, as in a mechanism involving copper reduction. Thus, although, no evidence for the assumed transient copper carbenoid species was obtained, the irreversible formation of catalytic amounts of copper(I) as the active species in the reaction, has been demonstrated.

Experimental

Synthesis of the substrate and the catalysts

Substrate Ia was made as previously described [9]. The catalysts were made by literature methods [10]. Analytical data were satisfactory.

Spectroscopic measaurements

ESR spectra were recorded on a Varian E9 instrument. Electronic spectra were recorded on a Varian 634 spectrophotometer with the cell compartment thermostated at 5 °C. ^{1}H NMR spectra were recorded with a Varian CFT-20 instrument operating at 80 MHz.

Acknowledgements

Financial support from the Ministero della Pubblica Istruzione is gratefully acknowledged.

References

1 A. Saba, Synthesis, 268 (1984); A Pusino, A. Saba and V. Rosnati, Tetrahedron, 42 (1986) 4319.
2 S.D. Burke and P.A. Grieco, Organic Reactions, Wiley, New York, 1979, Vol. 26, p. 361.
3 P.G. Gassmann and T. Nakai, J. Am. Chem. Soc., 93 (1971) 5897; 94 (1972) 2877.
4 H. Nozaki, S. Morinti, H. Takaya and R. Noyori, Tetrahedron. Lett., (1966) 5239 and refs. therein; M. Takebayashi, T. Ibata, H. Kohara and B. Hong Kim, Bull. Chem. Soc. Japan, 40 (1967) 2392; K. Ueda, T. Ibata, M. Takebayashi, Bull. Chem. Soc. Japan, 45 (1972) 2779.
5 R.G. Salomon and J.K. Kochi, J. Am. Chem. Soc., 95 (1973) 3300 and refs. therein.
6 H. Yokoi, Inorg. Chem., 17 (1978) 538.
7 H.A. Kuska, M.T. Rogers and R.E. Drullinger, J. Phys. Chem., 71 (1967) 109.
8 R. Abramovitch (Ed.): Reactive Intermediates, Vol. 1, Plenum Press, New York, 1980.
9 A. Pusino, V. Rosnati, C. Solinas and U. Vettori, Tetrahedron, 39 (1983) 2259.
10 J.A. Bertrand and R.I. Kaplan, Inorg. Chem., 5 (1966) 489.