

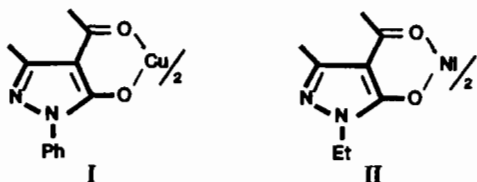
Benzophenone Sensitized Photochemistry of Cu(II) and Ni(II) Complexes with 4-Acylpyrazolones

G. E. BUONO-CORE* and G. LEON R.

Instituto de Química, Universidad Católica de Valparaíso, Casilla 4059, Valparaíso, Chile

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Although the sensitized photochemistry of several transition metal chelates has been studied in solution [1], no results have been reported so far for transition metal complexes with heterocyclic ligands such as 4-acyl-5-pyrazolones. In connection with our work with pyrazolone derivatives [2], and continuing with our search for new photocatalytic systems [3], we have studied the direct and sensitized photochemistry of transition metal complexes of 4-acyl-5-pyrazolones. Here we report some preliminary results obtained for the benzophenone sensitized photoreduction of bis(4-acetyl-1-phenyl-3-methyl-5-pyrazolonato)copper(II) (I), abbreviated Cu(AFMP)₂, and bis(4-acetyl-1-ethyl-3-methyl-5-pyrazolonato)nickel(II) (II), abbreviated Ni(AEMP)₂.



Experimental

Cu(AFMP)₂ and Ni(AEMP)₂ were prepared by the method used previously to prepare Ln(AFMP)₃ [4] and purified by recrystallization from methanol. Benzophenone (Merck) was used as received.

Photolyses were carried out using a Rayonet RPR-100 photoreactor equipped with lamps of 254, 300 and 350 nm and a merry-go-round unit for kinetic studies, and a 450 watt Hanovia mercury lamp with an immersion-type photocell for preparative work. The progress of the reactions was monitored by UV-Vis spectroscopy following the decrease in intensity for the absorption bands at 630 nm for Cu(AFMP)₂ and at 635 nm for Ni(AEMP)₂.

Quantum yields were determined in alcohol solutions contained in pyrex tubes and irradiated in the merry-go-round with 300 nm lamps for a

time sufficient to produce between 10 and 30% conversion of the complexes. To determine the concentration of the complexes, the photolysates were centrifuged for 10 min and filtered through a pipette packed with Celite before being analyzed by UV spectroscopy. For each series of experiments, the light intensity was determined using the actinometer benzophenone (0.05 M)/benzhydrol (0.1 M) in benzene with a reported quantum yield of 0.74 [5].

Results and Discussion

The direct photolysis of both Cu(AFMP)₂ and Ni(AEMP)₂ was carried out in different solvents and at different irradiation wavelengths. Only after prolonged irradiation (>24 h) with 254 nm light, could some decomposition be observed (less than 10% conversion) as shown by the slight decoloration of the original solutions and the formation of small amounts of metallic copper in the case of Cu(AFMP)₂, and Ni(0) in the case of Ni(AEMP)₂. This lack of efficiency shown by the complexes under direct irradiation contrasted drastically with the results obtained for the same systems when photolyzed in the presence of a triplet sensitizer such as benzophenone.

Irradiation of a methanol solution of Cu(AFMP)₂ (5.0 mM) containing benzophenone (6.5 mM) under nitrogen gave a suspension of metallic copper and a yellow solution after ~2.5 h. The yield of copper was determined by colorimetry to be 87%. Analysis of the photolysate showed the presence of the free ligand AFMPH (78%, by HPLC) and formaldehyde (45%, as its 2,4-DNPH derivative). Benzophenone was recovered almost quantitatively (98%) and no products derived from its photoreduction were detected. A similar reaction pattern was observed when ethanol or isopropanol were used as solvents with metallic copper being formed after 1.7 h in the former and 50 min in the latter solvent. In both cases oxidation products from the solvent were formed in 34% and 66% yields for acetaldehyde and acetone respectively. The sensitized photo-reaction was also attempted in solvents such as benzene, acetonitrile and chloroform but no photo-decomposition could be observed even after prolonged irradiation (>16 h).

When a methanolic solution of Ni(AEMP)₂ and benzophenone was irradiated under nitrogen through a pyrex filter, the initial light green color disappeared after 4 h to give rise to the deposition of metallic nickel. Analysis of the photolysate showed that benzophenone was not consumed during the reaction and that AEMPH (68%) and formaldehyde

* Author to whom correspondence should be addressed.

(56%) were the other products. The reaction in different solvents showed the same order of efficiency as that observed for $\text{Cu}(\text{AFMP})_2$, *i.e.* methanol < ethanol < 2-propanol. This was confirmed quantitatively by determining the quantum yields of $\text{Cu}(\text{AFMP})_2$ (Φ_{Cu}) and $\text{Ni}(\text{AEMP})_2$ (Φ_{Ni}) disappearance in different alcohols (Table 1). They were found to increase in the same order, indicating higher quantum yields in better hydrogen-donating solvents and also showing that $\text{Cu}(\text{AFMP})_2$ is more efficiently photoreduced than $\text{Ni}(\text{AEMP})_2$.

TABLE 1. Quantum Yields for the $\text{Cu}(\text{AFMP})_2$ (Φ_{Cu}) and $\text{Ni}(\text{AEMP})_2$ (Φ_{Ni}) Disappearance Sensitized by Benzophenone (0.1 M) in Alcohols

Solvent	Φ_{Cu}	Φ_{Ni}
Methanol	0.19	0.08
Ethanol	0.28	0.12
2-Propanol	0.34	0.21

In order to evaluate the efficiency of quenching of triplet benzophenone by complexes **I** and **II**, Φ_{Cu} (in methanol) and Φ_{Ni} (in ethanol) were determined at various concentrations of the quenchers. These values were used to plot $1/\Phi$ versus $1/[\text{ML}_2]$ according to a modified Stern–Volmer equation (eqn. (1)) [1]:

$$\frac{1}{\Phi} = \frac{1}{\alpha} + \frac{1}{\alpha\tau_{\text{B}}k_{\text{q}}[\text{ML}_2]} \quad (1)$$

where α is the fraction for intersystem crossing ($=1$ for Ph_2CO), τ_{B} is the lifetime for Ph_2CO triplet [6] and $[\text{ML}_2]$ is the concentration of the quencher. For $\text{Cu}(\text{AFMP})_2$, the plot gave a straight line ($r = 0.9849$) (Fig. 1a) from which k_{q} , the rate constant for quenching of benzophenone triplet by **I**, was determined from the slope ($=1/\tau_{\text{B}}k_{\text{q}}$) to be $k_{\text{q}} = (5.62 \pm 0.97) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. A slightly lower value was obtained from the plot of $1/\Phi_{\text{Ni}}$ versus $1/[\text{Ni}(\text{AEMP})_2]$ ($r = 0.9502$) (Fig. 1b) for the quenching of benzophenone triplet by **II** in ethanol with a k_{q} value equal to $(2.83 \pm 0.43) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

The results described above clearly demonstrate that benzophenone sensitizes the photodecomposition of $\text{Cu}(\text{AFMP})_2$ and $\text{Ni}(\text{AEMP})_2$ much more efficiently than the direct irradiation of these complexes. In both cases the final products are the same: the protonated ligand and the metal in oxidation state (0). The formation of intermediates with the metal in oxidation state +1 could not be confirmed conclusively. When the sensitized photolysis of $\text{Cu}(\text{AFMP})_2$ was carried out in the presence of triphenylphosphine (PPh_3) the formation of metallic copper was not observed. Instead, the reaction gave a yellowish solution which was stable under

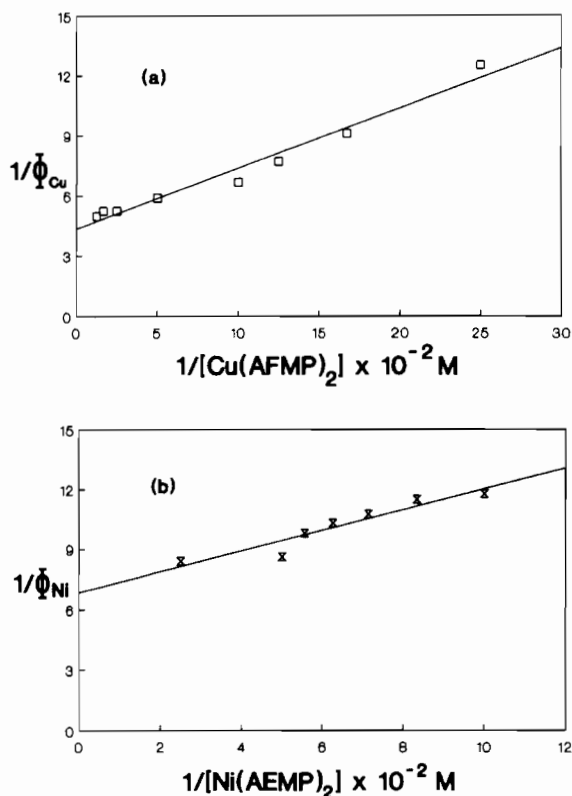


Fig. 1. Plot of $1/\Phi$ vs. $1/[\text{ML}_2]$ for quenching of benzophenone triplet by (a) $\text{Cu}(\text{AFMP})_2$ in methanol and (b) $\text{Ni}(\text{AEMP})_2$ in ethanol.

inert atmosphere but very sensitive to the presence of oxygen. This made the characterization of the possible intermediates difficult but showed that in the presence of strongly coordinating ligands the reaction could be stopped before the formation of the metals.

Stoichiometrically, the reduction of the metal ion $\text{M}(\text{II})$ to $\text{M}(\text{0})$, probably via $\text{M}(\text{I})$, must be coupled to the oxidation reaction of the solvent to carbonyl compounds. The mechanism of oxidation could be related to the way a ligand L abstracts a hydrogen to form the protonated ligand LH . The redox process must take place by a radical mechanism as suggested by the following observations. Firstly, the photoreduction did not occur in poor hydrogen donor solvents such as benzene, acetonitrile and chloroform. Secondly, the sensitized reaction takes place in alcohols with an order of efficiency that agrees with the ability with which these solvents can donate an α -hydrogen by a radical mechanism. This clearly suggests that a radical of the ligand $\text{L}\cdot$ might be the reactive species mediating the oxidation reaction by abstracting an α -H from the solvent.

It seems clear from the results reported here that in order to get a better understanding of the mechanisms involved in the process of sensitization,

the use of a wide variety of organic sensitizers as well as different metal complexes is necessary. This work is already in progress in our laboratory and will be discussed in a forthcoming article in more detail [7].

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