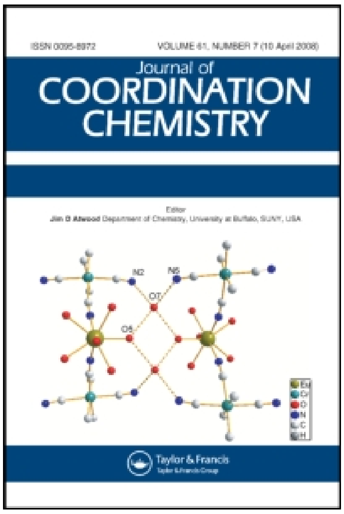

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TRIPLET STATE KETONE-SENSITIZED PHOTOCHEMISTRY OF Cu(II) AND Ni(II) COMPLEXES WITH 4-ACYLPYRAZOLONES

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Several aspects of the triplet state ketone-sensitized photoreduction of bis(4-acetyl-1-phenyl-3-methyl-5-pyrazolonato)-copper(II), and bis(4-acetyl-1-ethyl-3-methyl-5-pyrazolonato)-nickel(II) have been studied. It was found that the sensitized reduction was much more efficient than direct photolysis in hydrogen-donating solvents such as alcohols and tetrahydrofuran. The reaction products were identified as the metals in (0) oxidation state, the free protonated ligands and oxidation products derived from the solvents. The efficiencies of the reactions were quantitatively evaluated by determining the quantum yields, Φ, in different solvents and in the presence of different sensitizers. The results showed that the sensitized photoreduction was much more efficient in solvents with better hydrogen donating power, thus indicating that hydrogen abstraction is a key step in the reaction. A lack of correlation exists between the triplet energy levels of the sensitizers and the quantum yields of the photoreduction. The rate constants (k_q) for quenching of the benzophenone triplet state by the complexes were determined by Stern–Volmer type experiments. An overall mechanism for the sensitized photoreduction has been proposed.

Keywords: 4-Acetylpyrazolone, nickel(II), copper(II), ketones, photochemistry

INTRODUCTION

Transition metal ions and complexes of β-diketonates are known to be efficient quenchers of triplet states of a number of organic sensitizers[1–4] and several quenching mechanisms such as paramagnetic quenching,[1] energy transfer[3] and electron transfer[4] have been proposed. A careful evaluation of these studies seems to indicate that no single mechanism is capable of explaining the whole range of quenching reactions and that the overall mechanism is indeed a complex one. Although the sensitized photochemistry of transition metal 1,3-diketonates has been extensively studied over the past few years,[4] no results can be found in the literature for transition metal complexes with heterocyclic ligands such as 4-acylpyrazolones.

In connection with our work with pyrazolone derivatives,[5] and continuing with our search for new photocatalytic systems,[6] we have shown in a preliminary report that, bis(4-acetyl-1-phenyl-3-methyl-5-pyrazolonato)copper(II), I, Cu(AFMP)$_2$, and bis(4-acetyl-1-ethyl-3-methyl-5-pyrazolonato)nickel(II), I, Ni(AEMP)$_2$, can undergo benzophenone-sensitized photoreduction in hydrogen-donating solvents such as alcohols and tetrahydrofuran.[7] In order to gain more insight into the mechanism of the photoreduction, we have now undertaken a detailed study of the sensitized photochemistry of Cu(II) and Ni(II) complexes with 4-acyl- pyrazolones and results are reported here.

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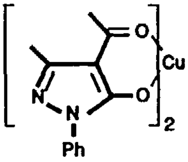

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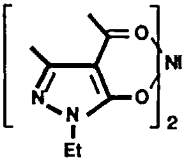

II

EXPERIMENTAL

Melting points were determined on a Mel-Temp capillary melting point apparatus. Ultraviolet and visible spectra were recorded on a Cary 219 spectrophotometer. Infrared spectra were measured on a Perkin-Elmer model 599-B spectrometer. HPLC was performed on a Waters 501 instrument equipped with a Waters 440 detector and using a Partisil PXS column.

Materials

Commercially available sensitizers were purified by distillation or recrystallization. $Cu(AFMP)_2$ and $Ni(AEMP)_2$ were prepared by the method used previously to synthesize $Ln(AFMP)_3$[8] and recrystallized from benzene. Solvents were of reagent grade and used without further purification. Tetrahydrofuran (THF) was distilled from lithium aluminum hydride and stored over sodium wire. Oxygen-free argon (Indura) was used as the inert gas in all the experiments.

Irradiations

Irradiations 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 and an immersion-type photocell (with a pyrex filter, 2 mm thickness) for preparative work. The progress of the reactions was monitored by electronic spectroscopy by following the decrease in intensity of the absorption band at 630 nm for $Cu(AFMP)_2$ and at 635 nm for $Ni(AEMP)_2$.

Photolysis procedure

A solution of the complex (ML_2) and sensitizer in *ca* 200 cm^3 of solvent under an argon atmosphere was irradiated in an immersion-type photocell through a pyrex filter ($\lambda > 290$ nm) with a 450 W Hanovia mercury lamp at ambient water temperature. The progress of the reaction was followed by examining the decrease in the visible absorption of ML_2. After irradiation was stopped, the photolysate was filtered through celite and the filtrate flash evaporated to remove the solvent. The residue was then analyzed by a combination of thin layer chromatography (on silica gel 60 F_{254}, Merck plates) and/or HPLC. When trapping of volatile products was required, the photolysate was distilled (immediately after irradiation was stopped) and the low-boiling fractions collected in a cold trap containing a 2,4-DNPH solution. If solids were formed, they were purified by recrystallization and characterized by m.p. and I.R.

Quantum yield determination

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 complex. The photolysates were centrifuged for 10 minutes and filtered through a pipette packed with celite before being analyzed by electronic spectroscopy. This procedure was necessary due to the formation of solids (suspensions) during the irradiations. For each series of experiments, the light intensity (I_0) was determined using the benzophenone (0.05 M)-benzhydrol (0.1 M) actinometer with a reported quantum yield of 0.74.[9] Corrections for the light absorbed by the complex (ML_2) at 330 nm were made using the following equation (*1*),

$$I_a = I_0AS_{330}/(AQ_{330} + AS_{330}) \text{ Einstein } l^{-1} s^{-1} \qquad (1)$$

where I_a = light intensity absorbed by the sensitizer, I_0 = light intensity determined from the actinometer, AS_{330} = optical density of the sensitizer at 330 nm and AQ_{330} = optical density of ML_2 at 330 nm.

RESULTS AND DISCUSSION

Sensitized photochemistry of Cu(AFMP)$_2$

The photoreaction of Cu(AMFP)$_2$ was first studied using a typical triplet sensitizer such as benzophenone. Irradiation (>290 nm) of a methanolic solution of Cu(AFMP)$_2$ (5.7 mmol) containing 6.5 mmoles of benzophenone under argon gave rise to the formation of a suspension of metallic copper in *ca* 3 h with the disappearance of the original green-blue colour. The percentage of Cu° (87%) was determined by colorimetric methods.[10] The yellow photolysate contained the free ligand AFMPH (78%) and formaldehyde (45%). Column chromatography (on silica gel) of the residue, obtained after solvent evaporation, showed that benzophenone was recovered almost quantitatively (98%) and also showed the absence of any product derived from the photoreduction of the sensitizer, such as benzopinacol and/or benzhydrol.

The effect of solvents on the photoreaction was also investigated. The photodecompositions of Cu(AFMP)$_2$ sensitized by benzophenone in ethanol and isopropanol caused the formation of metallic copper in 1.7 h and 50 min respectively. In both cases, Cu° was formed almost quantitatively (98% and 94%), whereas the yields of the free pyrazolone (AFMPH) were 82% and 73%, respectively. The oxidation products from the solvents, acetaldehyde (34%) for ethanol, and acetone (66%) for isopropanol, were determined as their 2,4-DNPH derivatives. In both solvents, the unreacted sensitizer was recovered in high yield. Under similar conditions, the benzophenone-sensitized photolysis in THF showed the same reaction pattern, *i.e.*, disappearance of the 630 nm absorption band and formation of Cu° after 1.5 h irradiation. However, in this case, the products derived from THF oxidation could not be isolated.

The photoreduction of Cu(AFMP)$_2$ could not be observed after 16 h irradiation in solvents such as benzene, acetonitrile or chloroform. In the latter solvent the colour of the solution changed to deep green, but without the formation of metallic copper.

It is possible that the reaction in chloroform leads to the formation of chlorine atoms which might modify the reaction pattern observed in alcoholic solvents or THF.

The photodecomposition of $Cu(AFMP)_2$ in the presence of different sensitizers was also investigated and the results are summarized in Table I. The following sensitizers (in decreasing order of efficiency) were effective in the photoreduction of the complex: anthrone, xanthone, biacetyl, acetophenone and benzil. In all these decompositions metallic copper and AFMPH were formed in nearly stoichiometric quantities and the sensitizers were recovered almost quantitatively. Small amounts of by-products were detected by chromatographic analyses in the reactions with anthrone, biacetyl and benzil; these compounds are known to easily decompose photolytically.[11]

Other sensitizers shown in Table I failed to photodecompose $Cu(AFMP)_2$ as indicated by UV and visual observations. With the exception of anthracene, the sensitizers were recovered quantitatively and no pyrazolone ligand or metallic copper was obtained. In the photolysis of a methanol solution containing $Cu(AFMP)_2$ and anthracene, the dimer of the latter was rapidly formed.[12] This was obtained after 16 h irradiation in 76% yield and trace amounts of other unidentified products were also detected by t.l.c.

TABLE I
Sensitized photodecomposition of $Cu(AFMP)_2$.

Sensitizer	Concentration ($M \times 10^3$)	Solvent	E_T[a] (kJ/mol)	Result[b]
Anthrone	3.6	EtOH	301	+
Xanthone	12.0	MeOH	310	+
Benzophenone	6.4	EtOH, MeOH IPA,[c] THF	289	+
Biacetyl	48.0	EtOH	230	+
Acetophenone	25.0	MeOH	310	+
Benzil	18.0	MeOH	225	+
Fluorenone	5.5	MeOH	223	−
Anthracene	5.7	MeOH	176	−
Pyrene	4.1	EtOH	201	−
Phenanthrene	11.7	EtOH	260	−
Perylene	0.4	EtOH	146	−

[a] Triplet energies are quoted from ref. 19. [b] A positive sign (+) indicates that metallic copper was formed. [c] IPA = 2-propanol.

Sensitized photochemistry of $Ni(AEMP)_2$

When a methanolic solution of $Ni(AEMP)_2$ and benzophenone was irradiated under argon through a pyrex filter ($\lambda > 290$ nm), the initial light green colour disappeared after *ca* 4 h, leading to the deposition of metallic nickel. When the photolysate was exposed to air, it caused the slow dissolution of the Ni(0) suspension to give a light green solution. Filtration of the photolysate through celite, immediately after the irradiation was stopped, gave a yellow solution showing no absorption at 635 nm. An HPLC analysis of the filtrate showed that benzophenone was not consumed during the reaction and that AEMPH (68%) and formaldehyde (56%) were the other products. The sensitized reaction in different solvents showed the same order of efficiency as that observed for $Cu(AFMP)_2$, *i.e.*, methanol > ethanol > 2-propanol.

The photoreduction of $Ni(AEMP)_2$ in ethanol was sensitized by xanthone, benzophenone and acetophenone in that order of decreasing efficiency (Table II), whereas other sensitizers such as fluorenone, 2-acetonaphthone and phenanthrene were inefficient.

TABLE II
Sensitized photodecomposition of $Ni(AEMP)_2$.

Sensitizer	Concentration ($M \times 10^3$)	Solvent	E_T[a] (kJ/mol)	Result[b]
Xanthone	12.5	EtOH	310	+
Benzophenone	6.2	EtOH, MeOH	289	+
Acetophenone	28.0	EtOH	310	+
Fluorenone	8.2	EtOH	223	−
2-Acetonaphthone	5.3	EtOH	248	−
Phenanthrene	13.2	EtOH	260	−

[a] Triplet energies are quoted from ref. 19. [b] Positive sign (+) indicates the formation of Ni(0) suspensions.

Quantum yield determination

In order to gain more insight into the sensitization mechanism, the quantum yields of $Cu(AFMP)_2$ (Φ_{Cu}) and of $Ni(AEMP)_2$ (Φ_{Ni}) in different solvents (Table III) and in the presence of different sensitizers (Table IV) were determined by monitoring the ML_2 absorption in the visible region. The average errors of these determinations were rather large (±30%), due mainly to small amounts of precipitates (see Experimental Section). However, these effects are common and compensated, relatively, in a series of samples irradiated under the same conditions. As shown in Table III, the quantum yields in different solvents were found to increase as the hydrogen-donating power of the solvent increased. This confirmed the order of efficiency observed in the sensitized reduction, *i.e.*, methanol < ethanol < 2-propanol.

TABLE III
Quantum yields of $Cu(AFMP)_2$ (Φ_{Cu}) and $Ni(AEMP)_2$ (Φ_{Ni}) photoreduction sensitized by benzophenone (0.1 M) in alcohols.

Solvent	Φ_{Cu}	Φ_{Ni}
Methanol	0.20	0.08
Ethanol	0.28	0.12
2-Propanol	0.34	0.21

In order to evaluate the nature of the quenching of triplet sensitizers by $Cu(AFMP)_2$, Φ_{Cu} in methanol was determined in the presence of anthrone, benzophenone, biacetyl, xanthone, acetophenone and benzil (Table IV). All these compounds had been shown to be efficient in sensitizing the photoreduction of the complex to metallic copper and the free ligand (see Table I). The concentration of the sensitizers was adjusted to absorb more than 98% of the incident light. In the case of biacetyl, in which the sensitizer absorbed only 68% of the light, the disappearance of $Cu(AFMP)_2$ was determined by normalizing the light absorbed to 100% (*1*), and Φ_{Cu} was calculated accordingly.

TABLE IV

Quantum yields of $Cu(AFMP)_2$ (Φ_{Cu}) and $Ni(AEMP)_2$ (Φ_{Ni}) disappearance in the presence of different sensitizers.

Sensitizer	Concentration (M)	Φ_{Cu}[a]	Φ_{Ni}[b]
Anthrone	0.1	0.24	
Benzophenone	0.1	0.20	0.12
Biacetyl	0.5	0.13	
Xanthone	0.1	0.12	0.18
Acetophenone	1.0	0.056	0.11
Benzil	0.1	0.049	

[a] In methanol. [b] In ethanol.

The quantum yields for the photoreduction of $Ni(AEMP)_2$, Φ_{Ni}, were also determined to be, for the sensitization with xanthone and acetophenone in ethanol, 0.18 and 0.11, respectively.

Kinetic analysis

The quantum efficiencies of $Cu(AFMP)_2$ disappearance, Φ_{Cu}, in methanol and in the presence of benzophenone were determined at various concentrations of the quencher (Table V). The results showed that Φ_{Cu} increased progressively in the $Cu(AFMP)_2$ concentration range $0.4–4.0 \times 10^{-3}$ M, to reach a nearly limiting value of 0.20 at $>8.0 \times 10^{-3}$ M. A plot of $1/\Phi_{Cu}$ *vs* $1/[Cu(AFMP)_2]^7$ according to (*2*) derived, after a kinetic analysis (steady state treatment) of the proposed mechanism (*vide infra*), gave a straight line (r = 0.9849) from which k_q, the rate constant for quenching of triplet benzophenone by $Cu(AFMP)_2$ was determined from the slope ($= 1/\beta\tau_B k_q$) to be $k_q = (5.62 \pm 0.97) \times 10^9\ M^{-1} s^{-1}$. The value for the intercept ($= 1/\beta$) of 4.37 also shows that the limiting quantum yield in the benzophenone-sensitized photolysis is 0.22, slightly higher but close to the experimental value of 0.20.

TABLE V

Average quantum yields of $Cu(AFMP)_2$ disappearance sensitized by benzophenone (0.1 M) in methanol (at 29°C).[a]

$[Cu(AFMP)_2] \times 10^3$ M	Φ_{Cu}	$1/[Cu(AFMP)_2]$	$1/\Phi_{Cu}$
0.4	0.08	2500	12.50
0.6	0.11	1670	9.09
0.8	0.13	1250	7.69
1.0	0.15	1000	6.67
2.0	0.17	500	5.88
4.0	0.19	250	5.26
6.0	0.19	167	5.26
8.0	0.20	125	5.00

[a] For each concentration of quencher three readings were taken to give the average quantum yields.

$$1/\Phi_{Cu} = 1/\alpha\beta + 1/\alpha\beta\tau_B k_q[Q] \quad (2)$$

α = fraction of intersystem crossing (for benzophenone $\alpha = 1$), [Q] = concentration of the quencher, ML_2, τ_B = lifetime of triplet benzophenone (in MeOH = 2.6×10^{-7}s),[13] k_q = quenching rate constant.

The quantum yield for the disappearance of $Ni(AEMP)_2$ Φ_{Ni}, was determined in ethanol and in the presence of benzophenone at different concentrations of the complex (Table VI). The limiting quantum yield ($\Phi_{Ni} = 0.12$ at 4×10^{-3} M) showed that the benzophenone sensitized photoreduction of $Ni(AEMP)_2$ is less efficient than that of $Cu(AFMP)_2$ (see Table V). Using the data from Table VI, a plot of $1/\Phi_{Ni}$ *vs* $1/[Ni(AEMP)_2]$[7] according to (*2*), gave a straight line with a correlation coefficient r = 0.9502, a slope of 5.5×10^{-3} and an intercept of 6.867 ± 0.513. The rate constant for quenching of triplet benzophenone by $Ni(AEMP)_2$ in ethanol was calculated to be $k_q = (2.83 \pm 0.43) \times 10^9\ M^{-1}\ s^{-1}$. On the other hand, the value for the intercept showed that the limiting quantum yield Φ_{Ni} of 0.15 obtained from the plot is slightly higher than the experimental value of 0.12.

TABLE VI

Average quantum yields of $Ni(AEMP)_2$ disappearance sensitized by benzophenone (0.1 M) in ethanol (at 28°C).[a]

$[Ni(AEMP)_2] \times 10^3$ M	Φ_{Ni}	$1/[Ni(AEMP)_2]$	$1/\Phi_{Ni}$
4.0	0.119	250	8.40
2.0	0.116	500	8.62
1.8	0.102	556	9.80
1.6	0.097	625	10.31
1.4	0.093	714	10.75
1.2	0.087	833	11.49
1.0	0.085	1000	11.77

[a] Average errors of Φ_{Ni} were ±25%.

Our earlier report[7] clearly showed that triplet benzophenone sensitized the photodecomposition of $Cu(AFMP)_2$ and $Ni(AEMP)_2$ much more efficiently than direct irradiation of these complexes and also demonstrated that the final products are in both cases the same: the protonated ligand, the oxidized solvent and the metal in oxidation state (0). The formation of a M(I) complex as the primary photoproduct was assumed but could not be confirmed conclusively due to the instability of the intermediates. When the sensitized photolysis of $Cu(AFMP)_2$ was carried out in the presence of strongly coordinating ligands such as triphenylphosphine or tri-*n*-butylphosphine, air-sensitive solutions were obtained but metallic copper was not formed.

Stoichiometrically, the reduction of M(II) to M(0), probably *via* M(I), must be coupled to the oxidation of the alcoholic solvents to carbonyl compounds. The mechanism of this oxidation could be related to the way a ligand L abstracts a hydrogen to form the protonated ligand L–H. That the redox process takes place by a radical mechanism is suggested by the following observations. First, the photoreduction did not take place in poor hydrogen-donor solvents such as benzene, cetonitrile or chloroform. Secondly, the reaction occurs in alcohols with an order of efficiency that agrees with the ability of these solvents to donate an α-hydrogen (but not a O–H hydrogen) by a radical mechanism. This can be taken as a clear indication that a radical of the ligand L is the reactive species mediating the oxidation reaction by abstracting an α-H from the solvent as shown in equations (*3*) to (*5*).

$$L\cdot + RCH_2OH \longrightarrow L{-}H + R\dot{C}HOH \tag{3}$$

$$2\,R\dot{C}HOH \longrightarrow RCH_2OH + RCH{=}O \tag{4}$$

$$L\cdot + M(L) \longrightarrow ML_2 \tag{5}$$

Considering the experimental data with proper caution, we can express a general mechanism for the photosensitized reduction of ML_2 by the following scheme, with benzophenone (Ph_2CO = BP) as the sensitizer.

$$Ph_2CO \xrightarrow[I_a]{h\nu} Ph_2CO(S_1) \xrightarrow[\alpha]{} Ph_2CO(T_1) \quad \alpha I_a \tag{6}$$

$$Ph_2CO^* + RCH_2OH \xrightarrow{k_r} Ph_2\dot{C}OH + R\dot{C}HOH \quad k_r[BP^*] \tag{7}$$

$$Ph_2CO^* \xrightarrow{k_e} Ph_2CO + h\nu\ (\Delta) \quad k_e[BP^*] \tag{8}$$

$$Ph_2CO^* + ML_2 \xrightarrow{k_q} [\text{complex}] \quad k_q[BP^*][Q] \tag{9}$$

$$[\text{complex}] + RCH_2OH \xrightarrow{k_p} \begin{array}{l} ML + L{-}H \quad k_p[C] \\ R\dot{C}HOH + Ph_2CO \end{array} \tag{10}$$

$$[\text{complex}] \xrightarrow{k_d} ML_2 + Ph_2CO \quad k_d[C] \tag{11}$$

In this scheme it is assumed that the species formed after the interaction of the triplet state of the sensitizer with ML_2 is a complex *C*.

A kinetic analysis of the reaction based on the scheme shown in (*6–11*) was developed to obtain the Stern–Volmer modified equation (*2*), where [C] is the concentration of complex *C*, [Q] is the concentration of ML_2, α is the fraction of intersystem crossing and [BP*] is the concentration of triplet benzophenone. This analysis suggests that the limiting quantum yield of ML_2 disappearance, Φ_{Cu}, arises from the partition of the complex *C* between a successful reduction (*10*) and an unsuccessful one (*11*), *i.e.*, k_d/k_p is determined to be 3.37 for Cu(AFMP)$_2$ and 5.87 for Ni(AEMP)$_2$, from the plots of $1/\Phi_M$ *vs* $1/[ML_2]$ using the data from Tables V and VI, respectively. These values are in agreement with the different reactivities shown by these complexes in the sensitized photoreduction.

Mechanism of Quenching

Several mechanisms could be operating in the sensitization step of the reaction. A scheme in which the triplet state of the sensitizer is mediating a hydrogen transfer from the solvent to ML_2 is attractive if one considers the typical reactions of triplet state benzophenone.

$$Ph_2CO^* + RCH_2OH \longrightarrow Ph_2\dot{C}OH + R\dot{C}HOH \qquad (12)$$

$$Ph_2\dot{C}OH + ML_2 \longrightarrow Ph_2CO + ML + L\text{–}H \qquad (13)$$

However, this mechanism seems unlikely if one takes into account the fact that hydrogen abstraction by triplet benzophenone is a relatively slow process ($k = 1.8 \times 10^6\ M^{-1}\ s^{-1}$).[14]

Although it could be assumed that the sensitized photodecomposition occurs through an undefined excited state of ML_2 by an internal redox mechanism, the evidence presented in Table IV is against a classical mechanism of triplet energy transfer from the excited state of the sensitizers to the ground state of ML_2. For example, the order of efficiency for sensitization of $Cu(AFMP)_2$ (anthrone > benzophenone > biacetyl > xanthone > acetophenone > benzil) does not agree with the order of triplet energies of the sensitizers. It is also apparent that none of these ketones possesses a singlet state energy high enough to successfully activate the CTTM transition band of $Cu(AFMP)_2$. The same argument can be used for $Ni(AEMP)_2$.

An energy transfer to d–d states of the complexes or to low-energy charge transfer states is also energetically possible and cannot be completely excluded. However, we have demonstrated[7] that a direct excitation of the d–d transition band (in the absence of sensitizers) does not lead to a photoreduction of the metal complexes.

Several investigations have been published related to the mechanism of sensitized reactions of metal complexes. For example, the luminescent excited state of Ru(II) polypyridine complexes is quenched by various metal ions and complexes by either electron transfer or energy transfer mechanisms depending on the nature of the quenchers.[15–17] This particular state of the ruthenium(II) complexes is unique in that it can act as an electron donor as well as an acceptor with a wide range of quenchers. On the other hand, Wilkinson[3] and others[18] observed that the quenching efficiencies of triplet state of organic compounds by iron and other coordination complexes are dependent on the relative energy levels of the interacting species, which suggests that the quenching mechanism involved an energy transfer. Earlier, Hammond and coworkers[2] had shown that several transition metal complexes efficiently quench a variety of sensitizers, but that the quenching rate constants (k_q) do not correlate with the triplet energy levels of the sensitizers. They concluded that either the complexes possess excited states to which they can be promoted by an energy transfer or the quenching by these complexes does not involve this type of process.

In summary, for the reasons and experimental evidence presented here, it is believed that the sensitization mechanism for the photoreduction of 4-acylpyrazolone complexes does not occur exclusively by an energy transfer process. On the basis of the results of this investigation alone it would be premature to propose a definite mechanism. Furthermore, it should be recognized that it is unlikely that one single mechanism could explain the whole range of experimental observations for these reactions, and that the overall mechanism may actually involve a complex sequence of charge transfer, electron exchange and hydrogen abstraction. Further studies using flash photolysis techniques to determine directly the rate constants for quenching might reveal more detail concerning this process.

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