# Scavenging of 1,4-Biradicals by Bis(acetylacetonato)copper(II). The Importance of Paramagnetic Effects<sup>1</sup>

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 $Cu(acac)_2$  is shown to interact with the triplet biradical  $(CH_3)_2CCH_2CH_2C(OH)C_6H_5$  promoting its intersystem crossing to the product forming singlet species. The scavenging of the biradicals does not lead to any new products, but the product ratios (cyclobutanol and acetophenone) are modified, showing that paramagnetic scavengers can exert some control on the conformation of the nascent singlet biradical. The rate of scavenging in methanol at 27 °C is  $2.0 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>, as determined by laser flash photolysis.

#### Introduction

Several reactions of the biradicals generated in the Norrish type II reaction (Scheme I) have been the subject of recent studies.<sup>3-14</sup> In general, it has been observed that reactions of triplet biradicals with diamagnetic subtrates lead to typical monoradical behavior.<sup>3,4,12-14</sup> The reactions with paramagnetic quenchers, such as nitroxides,<sup>11,14</sup> and oxygen,<sup>6,15</sup> frequently lead to rather distinct behavior that does not reflect monoradical properties, but rather the spin selection rules involved in the interaction of the quencher with the triplet biradical. It has been  $proposed^{6,11,14,16}$  that paramagnetic quenchers assist intersystem crossing in the biradical and that they can control product ratios by leading to intersystem crossing from average geometrical configurations different from those in which the process occurs spontaneously.

Apparently there are no reports in the literature on the scavenging of type II biradicals by metal ions or their complexes. Copper complexes can potentially scavenge biradicals by two different mechanisms: chemical reaction (probably redox) or paramagnetic quenching; the latter would reflect the free radical characteristics of copper(II) complexes.<sup>17</sup> The study of these processes can be expected to throw light on the unusual characteristics of the interaction of biradicals with paramagnetic species. In addition, it may be possible to understand in more detail the

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Scheme I



way in which copper(II) compounds interact with excited states,<sup>18</sup> since one of the possible reaction paths, namely energy transfer, is not available in the case of biradicals.

The involvement of copper complexes in photochemical reactions has been the subject of a recent review,<sup>19</sup> however, the role of the paramagnetic properties of copper(II) complexes has not been given any serious consideration. In this paper we report the results of a study of the scavenging of type II biradicals by the complex bis(acetylacetonato)copper(II), Cu(acac)<sub>2</sub>. The combination of quantum yield and laser flash photolysis studies leads to a detailed understanding of the role of Cu(II) in the system. The biradical chosen for detailed study was the one from  $\gamma$ -methylvalerophenone, which in earlier studies<sup>6,7,11,14</sup> has been shown to be a good choice because of the short lifetime of the triplet state<sup>7,20</sup> in comparison with the biradical lifetime (e.g.,  $\tau_{\rm B} = 97$  ns in methanol).<sup>7</sup>

## Results

Laser Flash Photolysis. Our experiments were carried out under oxygen-free conditions using the pulses from a nitrogen laser (337.1 nm, 8 ns, up to 10 mJ) for excitation. Biradical absorptions (Scheme I) were monitored at 415 nm.<sup>21</sup> The biradical lifetime,  $\tau_{\rm B}$ , is 97 ns in methanol and shorter in the other solvents examined.<sup>7,22</sup> The concen-

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**Figure 1.** Determination of  $k_{T}$  in methanol from the effect of Cu(acac)<sub>2</sub> on the biradical lifetime (27 °C).

trations of  $Cu(acac)_2$  necessary for the study are usually high enough (up to 5 mM) that UV screening at 337.1 nm is inevitable. The bimolecular rate constant  $k_{\rm T}$  for the trapping of the biradical by the complex can be obtained from a plot of  $\tau_{B}^{-1}$  vs. the concentration of Cu(acac)<sub>2</sub>. Figure 1 shows the corresponding plot in methanol as solvent and leads to  $k_{\rm T} = (1.98 \pm 0.20) \times 10^9 \,{\rm M}^{-1} \,{\rm s}^{-1}$  at 27 °C. Thus, when the concentration of  $Cu(acac)_2$  is 5 mM, about 50% of the intersystem crossing is the result of a copper-induced process. Similar measurements in 10% water/acetonitrile led to  $k_{\rm T} \sim 0.5 \times 10^9 {\rm M}^{-1} {\rm s}^{-1}$ . No consumption of Cu(acac)<sub>2</sub> was observed in these experiments, even after prolonged exposure to the laser beam. In benzene it was not possible to obtain  $k_{\rm T}$  as a result of the short biradical lifetime compounded by the lower solubility of  $Cu(acac)_2$  in this solvent.

A detailed examination of the transient spectrum following biradical decay did not reveal the presence of any new transient, except for relatively weak signals at  $\lambda < 400$ nm, which can be attributed to acetophenone enol,  $CH_2 = C(OH)C_6H_5$ .

Quantum Yield Studies. Quantum yield measurements are rather difficult in this particular system because the absorption spectrum of Cu(acac)<sub>2</sub> overlaps extensively with that of the parent ketone,  $\gamma$ -methylvalerophenone. It is also important to use  $\lambda > 300$  nm, where, even if UV screening is unavoidable, the light absorbed by Cu(acac)<sub>2</sub> does not lead to its photodecomposition. Depending upon the experiment, the light used was mainly the 334 and/or 365/6-nm mercury lines. At these wavelengths Cu(acac)<sub>2</sub> is photostable.<sup>23,24</sup>

The reaction products in the presence of enough Cu-(acac)<sub>2</sub> to quench over 50% of the biradicals were those characteristic of the Norrish type II reaction, i.e., acetophenone, 2-methylpropene and the corresponding cyclobutanol (see Scheme I). It is important to note that acetylacetone (acacH), one of the expected products if triplet quenching or reduction of Cu(acac)<sub>2</sub> took place, was absent among the products of low conversion photolysis. In quantitative terms  $\Phi(acacH) \ll 0.01$ . Metallic copper, or the polymeric black precipitate which is common in other systems,<sup>18,23</sup> was not observed at all. In fact, no change in the concentration of Cu(acac)<sub>2</sub> was detected even when the concentration of  $\gamma$ -methylvalerophenone converted to products was several times larger than the concentration of Cu(acac)<sub>2</sub>.

In a series of experiments with  $Cu(acac)_2$  concentrations in the 0–0.006 M range in methanol and using  $\gamma$ -methyl-

TABLE I: Relative Yields of Cyclobutanols and Acetophenone in the Irradiation of  $\gamma$ -Methylvalerophenone in the Presence of Cu(acac)<sub>2</sub> in Methanol at 27 °C

-					
	[Cu(acac) <sub>2</sub> ], mM	CB/ ACP	Φ <sub>T</sub>	α	$\frac{\Phi_{CB(1+\alpha)}}{(\Phi_{CB} + \Phi_{ACP})}$
	0	0.064	0	0	0.060
	0.5	0.065	0.088	0.097	0.067
	1.0	0.066	0.162	0.193	0.074
	2.0	0.071	0.279	0.39	0.092
	2.5	0.078	0.324	0.48	0.107
	4.0	0.077	0.437	0.78	0.127
	5.0	0.086	0.490	0.96	0.155
	6.0	0.094	0.538	1.16	0.186
	8.0	0.111	0.610	1.56	0.256
	10.0	0.105	0.658	1.92	0.277

valerophenone 0.055 M, we introduced suitable corrections to account for the light absorbed by  $Cu(acac)_2$ . Under these conditions up to 55% of the biradicals were scavenged. We observed that the corrected quantum yield of acetophenone formation was essentially constant within experimental error (±10%).

In contrast to the above observation, photolysis of butyrophenone in the presence of Cu(acac)<sub>2</sub>, quickly deposited a black precipitate of Cu(acac)(I) polymers, which turn to metallic copper upon continued irradiation.<sup>25</sup> The reaction pattern is similar to that of the benzophenone sensitized photolysis<sup>18</sup> and yields acetylacetone. As in earlier studies,<sup>18,23</sup> the formation of this precipitate can be prevented by addition of triphenylphosphine and is fully consistent with triplet quenching playing a dominant role in the case of butyrophenone. While the details of triplet quenching studies will be reported in detail elsewhere, it is worthwhile to point out that the  $k_q$  value of  $6.6 \times 10^9$ M<sup>-1</sup> s<sup>-1</sup> derived from these studies is in good agreement with the value of 7.6  $\times$  10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> for propiophenone, obtained using laser flash photolysis.

The importance of triplet quenching in the case of butyrophenone is directly related to its long triplet lifetime<sup>7</sup> and leads to marked decreases in the acetophenone yields. Biradical quenching (that presumably also takes place) is not expected to change the acetophenone yield significantly (see experiments above).

We have shown in earlier work that the changes in the yield of acetophenone with the scavenger concentration can be correlated with  $k_{\rm T}\tau_{\rm B}^{6,11,26}$  In fact, there are a number of examples (including oxygen in benzene)<sup>6,15</sup> where the scavenger enhances the yields of photoreaction. The observation of such an enhancement is usually accepted as conclusive evidence for biradical scavenging by a mechanism that can control the partition of the biradical into products.<sup>13</sup> Unfortunately, no directly detectable enhancement can be expected in the case of Cu(acac)<sub>2</sub> because its solubility is rather limited in nonpolar solvents, the only ones in which the experiment mentioned above would be viable, since all biradicals already proceed to products in polar media.<sup>12</sup>

An alternative approach that can be used and that also avoids the use of extensive corrections to account for UV screening is to base the experiments on the cyclobutanol-to-acetophenone (CB/ACP) ratios (Scheme I). The effect of  $Cu(acac)_2$  on CB/ACP was examined in methanol solvent; the CB/ACP ratio was found to increase

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<sup>(25)</sup> We note that experiments with  $\gamma$ -methylvalerophenone at high conversions (e.g., 20-60%) do lead to the formation of acacH and copper-containing precipitates. These can be attributed to the photoexcitation of acetophenone generated in the Norrish type II process (see Scheme I).

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markedly in the presence of the copper complex. Table I illustrates the ratios obtained for different concentrations of Cu(acac)<sub>2</sub>. We note that reagents that only quench the triplet state cannot change CB/ACP. This group of experiments was carried out using a 360-nm cut-off filter, so that the incident light absorbed can be regarded as the 365/6-nm mercury lines exclusively. Cu(acac)<sub>2</sub> was not consumed in this experiments and only a trace of acacH ( $\Phi \ll 0.01$ ) could be detected. A few experiments using a 334-nm interference filter agreed well with the data in Table I, although they required substantially longer irradiation times.

#### Discussion

We propose that  $Cu(acac)_2$  interacts with the transients involved in the Norrish type II reaction in two different ways. (a) Triplet quenching  $(k_q)$  leads to the generation of acacH and copper precipitates. Naturally, this is the only reaction path available in the cases of acetophenone and propiophenone, where the Norrish type II reaction is not possible, and it seems to be the predominant process in the case of butyrophenone which has a relatively long lived triplet.<sup>7</sup> (b) Biradical scavenging does not lead to any new products, but it does change the partition of the biradical into products. Reactions 1–9 illustrate the mech-

$$K \xrightarrow{h\nu} \xrightarrow{ISC} {}^{3}K$$
 (1)

$$^{\tau_{T}} \xrightarrow{3} B$$
 (2)

 ${}^{3}K + Cu(acac)_{2} \xrightarrow{q} reduction products$  (3)

$${}^{3}B \xrightarrow{\tau_{B}}{}^{1}B_{a}$$
 (4)

$${}^{1}B_{a} \rightarrow CH_{3}COPh + olefin$$
 (5)

$$B_a \rightarrow cyclobutanol$$
 (6)

$${}^{3}\mathrm{B} + \mathrm{Cu}(\mathrm{acac})_{2} \xrightarrow{\kappa_{\mathrm{T}}} \mathrm{Cu}(\mathrm{acac})_{2} + {}^{1}\mathrm{B}_{\mathrm{b}}$$
 (7)

$$^{1}B_{b} \rightarrow CH_{3}COPh + olefin$$
 (8)

$${}^{1}B_{b} \rightarrow \text{cyclobutanol}$$
 (9)

anism proposed, where K stands for ketone, B for biradical (see Scheme I), and the superscript indicates the multiplicity.

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The subscripts a and b indicate singlet biradicals generated via spontaneous and  $Cu(acac)_2$  induced intersystem crossing, respectively. A model for biradical reactions proposed recently<sup>14</sup> suggests that singlet biradicals can "remember" the structure in which they were initially generated. This memory is reflected in different product ratios for singlet biradicals of different origin; thus the need to label them depends on whether their generation takes place in reactions 4 or 7. We note that our mechanism excludes one of the rather common biradical reactions, i.e., the reabstraction (or back-transfer) of the hydroxylic hydrogen to regenerate the parent ketone (see Scheme I). This process has been shown to be unimportant in polar hydrogen bonding solvents like the ones used here.<sup>4,12,13,27,28</sup>

The change in product ratios (i.e., CB/ACP) shown in Table I coupled with the value measured by flash photolysis of  $k_{\rm T}$  of  $\sim 2 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup> is a clear indication of biradical scavenging, as well as of induced intersystem crossing. Triplet quenchers cannot modify CB/ACP, since



Figure 2. Plot according to eq 14 for the data in methanol at 27 °C (correlation coefficient = 0.992).

they would only change the quantum yield of biradical formation, not the product ratio derived from the biradical. A similar argument applies to biradical scavengers that only interact with one radical site (i.e., monoradical type of behavior); these will simply remove some biradicals from the system but would not influence the product ratios which result from independent reactions of the remaining biradicals.

Further support for the idea of biradical scavenging not leading to any new products comes from the near constancy of the acetophenone quantum yields (from  $\gamma$ -methylvalerophenone) and from the fact that the formation of copper (noted visually) seems to be inversely proportional to the triplet lifetime; thus, in the limiting cases, Cu<sup>o</sup> and acacH are efficiently generated by acetophenone, but are absent in the case of  $\gamma$ -methylvalerophenone experiments at low conversion (i.e., before acetophenone starts to accumulate). Experiments of this type have been frequently used to establish whether a certain process involves a biradical or a triplet pathway.<sup>5,6,10,11</sup>

From a kinetic point of view the dependence of CB/ACP on the concentration of  $Cu(acac)_2$  is not expected to follow a simple relationship. The corresponding quantum yields, in the absence of triplet quenching, will be given by eq 10 and 11

$$\Phi_{\rm CB} = \Phi_{\rm T} \, \frac{k_9}{k_8 + k_9} + (1 - \Phi_{\rm T}) \, \frac{k_6}{k_5 + k_6} \tag{10}$$

$$\Phi_{\rm ACP} = \Phi_{\rm T} \, \frac{k_8}{k_8 + k_9} + (1 - \Phi_{\rm T}) \, \frac{k_5}{k_5 + k_6} \qquad (11)$$

where  $\Phi_{T}$  is the fraction of biradicals trapped

$$\Phi_{\rm T} = \frac{k_7 [{\rm Cu}({\rm acac})_2]}{k_4 + k_7 [{\rm Cu}({\rm acac})_2]} \tag{12}$$

 $\Phi_{\rm T}$  can be easily calculated from the laser flash photolysis data; in methanol the biradical lifetime,  $\tau_{\rm B}$ , is 97 ns ( $\tau_{\rm B} = k_4^{-1}$ ) and  $k_7 = 2.0 \times 10^9 \,{\rm M}^{-1} \,{\rm s}^{-1}$  at 27 °C. If we now define  $\alpha$  according to eq 13, then eq 14 provides a convenient linear representation that combines the quantum yield and laser flash photolysis data.

$$\alpha = \frac{\Phi_{\rm T}}{1 - \Phi_{\rm T}} \tag{13}$$

$$\frac{\Phi_{\rm CB}(1+\alpha)}{\Phi_{\rm CB}+\Phi_{\rm ACP}} = \frac{k_6}{k_5+k_6} + \frac{\alpha k_9}{k_8+k_9}$$
(14)

Figure 2 shows a plot according to eq 14 which leads to  $k_6/(k_5 + k_6) = (0.060)$  and  $k_9/(k_8 + k_9) = 0.118 \pm 0.011$ . The value of  $k_6/(k_5 + k_6)$  is hardly surprising since this value (based on Wagner's reports)<sup>4</sup> was taken as a reference in the absence of Cu(acac)<sub>2</sub> to calibrate our chromatograph.

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The value for  $k_9/(k_8 + k_9)$  obtained from the slope in Figure 2 clearly shows that the fraction of biradicals that yields cyclobutanols is approximately doubled for those biradicals which undergo intersystem crossing assisted by Cu(acac)<sub>2</sub>. Thus, the present system provides another example where paramagnetic interactions exert considerable control on the reaction pathways by which a biradical decays. The singlet biradical produced via intersystem crossing must be extremely short lived (10<sup>-10</sup> to 10<sup>-11</sup> s) in order to retain some conformational memory reflecting the history of the precursor triplet biradical.<sup>14</sup>

It is rather interesting that paramagnetic interactions with  $Cu(acac)_2$  would favor cyclization. While the magnitude of the rate constants clearly indicates that all conformations must be trapped,  $Cu(acac)_2$  seems to show some preference for those biradicals in a cisoid conformation, or even a propensity to exert some control over the conformation distribution. While not strictly required by the data, the biradicals in a cisoid conformation could conceivably coordinate to the copper center more easily.

#### **Experimental Section**

Materials.  $\gamma$ -Methylvalerophenone was a Fluka product, and all other ketones were obtained from Aldrich. They were usually treated in an alumina column and distilled prior to use. All those capable of undergoing the Norrish type II reaction were shown to be free from acetophenone (VPC). Methanol (Aldrich, Gold Label), acetonitrile (Baker, Spectrograde), and benzene (Aldrich, Gold Label) were used as received.

Laser Flash Photolysis. All our experiments were carried out in deaerated 1-mL samples contained in Suprasil sample cells. Our laser facility uses the pulses (337.1 nm, ~8 ns, up to 10 mJ) of a Molectron UV-24 nitrogen laser for excitation. The system has been fully interfaced with a PDP11/03L computer that controls the experiments and provides suitable data processing, storage, and hard-copy facilities. Data acquisition is carried out via a Tektronix R7912 transient digitizer. Further details have been given elsewhere.<sup>29</sup> Quantum Yield and Preparative Studies. These experiments were carried out using a 150- or 450-W Hanovia high-pressure mercury lamp for excitation. In the studies of the CB/ACP ratio, a Schott WG-360 filter was used; under those conditions the 365/6 mercury lines are the main ones used for excitation. In preparative experiments, particularly where the effect of conversion was examined, only a Pyrex filter was used. In this case the main excitation wavelength is the 334-nm line, with some contribution at 313 and 365/6 nm. We note that  $Cu(acac)_2$  is photostable in this spectral region.

Corrections for UV screening were based on the extinction coefficients at 334 nm when a Pyrex cutoff was used as well as when the interference filter at his wavelength was employed. Quantum yield studies were carried out by simultaneous irradiation of several samples using a "merry-go-round" system.

The concentration of  $Cu(acac)_2$  was monitored spectrophotometrically using a Cary 219 spectrometer and all other components by gas chromatography on OV-101 or SE-30 columns in chromatographs using flame ionization detectors.

Preparative experiments were carried out as in earlier studies.<sup>18</sup> In the case of  $\gamma$ -methylvalerophenone, (0.1 M) irradiation for up to 3 h with close to 20% conversion in the presence of up to 5.1 mM Cu(acac)<sub>2</sub> did not lead to any precipitate. All experiments were carried out under oxygen-free conditions. The products of the reaction were characterized by GC-MS using a Hewlett-Packard 5992B instrument. It was of particular interest to establish that the cyclobutanol GC signal corresponded solely to this species. The mass spectrum in the presence of Cu(acac)<sub>2</sub> [176(M<sup>+</sup>), 174, 120(base), 105,78,77] was identical with that obtained in the absence of the Cu(II) substrate.

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# Thermodynamic Transfer Functions of Nonionic Solutes between Immiscible Liquid Phases. Transfer of Some Secondary Alcohols from n-Octane to Water at 298.15 K

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Calorimetric determinations of the thermodynamic transfer functions  $(\Delta G^{\circ}_{t}; \Delta H^{\circ}_{t}; \Delta S^{\circ}_{t})$  of 2-propanol, 2-butanol, 2-pentanol, 2-hexanol, and ethanol from *n*-octane to water at 298.15 K have beem made. The resulting data show the same general behavior observed previously for unbranched monohydric alcohols. The thermodynamic transfer quantities of both normal and secondary alcohols have been analyzed in terms of polar and nonpolar contributions. This analysis suggests that, in the transfer process of a nonpolar solute, cavitation is the main factor driving the process itself.

#### Introduction

This work is an extension of an investigation concerning the transfer process of polar nonionic molecules of various homologous series from an apolar organic solvent to water. Such solute molecules are ideal substrates for investigating the effect of molecular size and nature on the different interactions driving the distribution process. In addition, a systematic study of the model molecule distribution can be a very useful source of information for a better understanding of more complicated systems. It is, for instance, an interesting task to explain the energetics of many biochemical phenomena which can be considered as the transfer processes of complex molecules from nonpolar to aqueous environments.<sup>1</sup>