

MECHANISTIC STUDIES OF THE SENSITIZED PHOTOREDUCTION OF BIS(ACETYLACETONATO)COPPER(II) BY PHENYLALKYL KETONES

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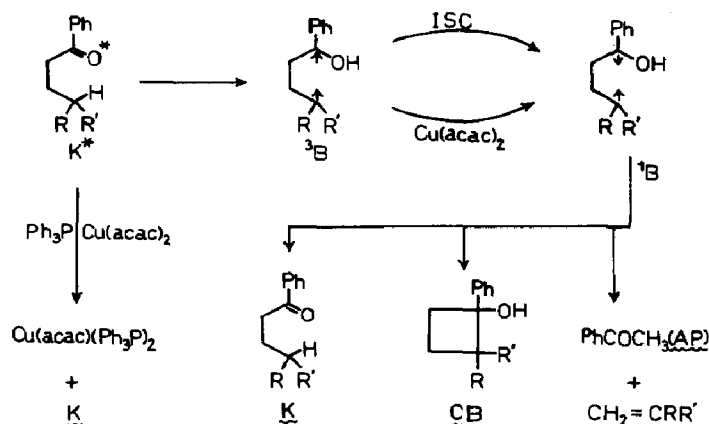
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Summary

Bis(acetylacetonato)copper(II) ($\text{Cu}(\text{acac})_2$) interacts with both the triplet excited state and the triplet biradical of phenylalkyl ketones which undergo the Norrish type II reaction. Mechanistic studies by static quenching methods show that the triplet biradicals interact with the paramagnetic copper species, leading to the preferential formation of cyclobutanols without the formation of new products; in the presence of Ph_3P the former interaction causes the known reduction of $\text{Cu}(\text{acac})_2$ to $\text{Cu}(\text{acac})(\text{Ph}_3\text{P})_2$, with a rate constant of about $6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. It is shown that Ph_3P interacts with one reactive intermediate, the triplet excited state ketone. The results of extensive kinetic analysis strongly support the proposed reaction mechanism.

1. Introduction

The interactions of the triplet biradicals generated in the Norrish type II reaction [1 - 3] with diamagnetic [4, 5] and paramagnetic [6 - 9] substrates have been the subject of recent studies. The interactions involving paramagnetic substrates such as nitroxides [6, 7] and oxygen [8, 9] promote the intersystem crossing (ISC) of the triplet to the singlet biradical and also, in due course, modify the product distribution [6 - 8]. Such a modification may reflect the operation of the spin selection rules during the interaction of the triplet biradical with the paramagnetic species. Recently, the first example was reported [10] of the interactions of triplet biradicals (*e.g.* from γ -methylvalerophenone) with paramagnetic metal complexes such as bis(acetylacetonato)copper(II) ($\text{Cu}(\text{acac})_2$). It has been shown that $\text{Cu}(\text{acac})_2$ enables the triplet biradical to undergo ISC selectively to the singlet state, favouring cyclobutanol (CB) formation over fragmentation to give acetophenone (AP) and isobutene.



Scheme 1.

Cu(acac)_2 also quenches the triplet excited state of aromatic ketones and is itself reduced to Cu(acac) polymers by a charge transfer mechanism [11 - 14]. Owing to this complication, only aromatic ketones possessing short triplet excited state lifetimes, such as γ -methylvalerophenone, could be studied kinetically, since their quenching by Cu(acac)_2 is inefficient and leaves ample opportunity for the generation of biradicals. This difficulty has now been overcome since we have shown that transient Cu(acac) can be stabilized with Ph_3P to form $\text{Cu(acac)(Ph}_3\text{P)}_2$ which is soluble and stable. The kinetics and the mechanism of the quenching of triplet state aromatic ketones by Ph_3P have been delineated previously [15], in which it was also shown that biradicals do not react with Ph_3P . These results permit us to investigate simultaneously the interactions of paramagnetic Cu(acac)_2 with the triplet excited states and the triplet biradicals with different lifetimes derived from phenylalkyl ketones in kinetic experiments by static quenching methods. Butyrophenone, valerophenone and γ -methylvalerophenone were chosen for the mechanistic studies since their biradical lifetimes in methanol are about 100 ns but their triplet excited state lifetimes vary considerably, being 70 ns, 16 ns and 4.7 ns respectively [16]. The quenching of the AP triplet state was also studied for comparison.

2. Experimental details

2.1. General conditions and materials

Butyrophenone, valerophenone, AP (all Aldrich) and γ -methylvalerophenone (Fluka) were distilled and their purity was examined by gas phase chromatography (GC) analysis. Methanol was distilled twice. Cu(acac)_2 was recrystallized three times from benzene [11].

UV spectra were obtained using Specord UV-visible (Zeiss) and VSU-2P (Zeiss) spectrophotometers. GC analysis was performed on a Chrom IV flame ionization detector with a 5% Carbowax 20 m column, using nonanol-1 as an internal standard. A JMS-D-100 (JOEL) mass spectrometer was used for the GC-mass spectroscopy (MS) analysis.

2.2. Irradiation techniques

A series of samples placed in phototubes was simultaneously irradiated in a 'homemade merry-go-round' machine. An HBO 200 W high pressure mercury lamp (Narva) with a combination of BC-7 (Mashpriborintog, U.S.S.R.) and Wood's filters was used to isolate the 365 nm mercury line. A methanol solution (4 ml) containing aromatic ketones, PPh_3 (0.01 M) and $\text{Cu}(\text{acac})_2$, ranging from 1×10^{-3} to 8×10^{-3} M, was purged with purified argon and irradiated. After irradiation, the samples were analysed for a decrease in absorbance of $\text{Cu}(\text{acac})_2$ at 630 nm in cells of path length 2 cm. These samples were analysed by GC to determine the AP and CB concentrations against the internal standard. The products were characterized by GC-MS analysis.

A solution of butyrophenone in benzene ($\Phi = 0.34$) was used as an actinometer [17]. The intensity I_0 of the incident light was $0.055 \text{ einstein l}^{-1} \text{ h}^{-1}$. Irradiation times were chosen to give about 5% ketone conversion. The correction for the absorption of the 365 nm excitation line by $\text{Cu}(\text{acac})_2$ was made using the equation [18]

$$I_k = I_0 t \frac{A_k}{A_k + A_{\text{Cu}}} \{1 - 10^{-(A_k + A_{\text{Cu}})}\}$$

where A_k and A_{Cu} are the absorbances at 365 nm for the ketone and $\text{Cu}(\text{acac})_2$ respectively and I_k is the intensity of light absorbed by the ketone in the presence of $\text{Cu}(\text{acac})_2$. $\text{Cu}(\text{acac})_2$ -methanol solutions are photostable during irradiation in this spectral region [11 - 13]. The quantum yields Φ_{AP} and Φ_{CB} for the formation of AP and CB and the quantum yield Φ_{Cu} for the disappearance of $\text{Cu}(\text{acac})_2$ are listed in Table 1.

For valerophenone, several series of irradiations were carried out with fixed Ph_3P concentrations in the range 0.000 - 0.025 M. Irradiation of those solutions for which $[\text{Ph}_3\text{P}] = 0$ caused a black precipitate to form. 0.05 M deoxygenated Ph_3P solution (1 ml) was added to the tube by using a syringe and after 10 - 15 min gave a clear solution for UV examination. For each series, the Φ_{AP} were determined and the standard Stern-Volmer relation $\Phi_{\text{AP}}^0/\Phi_{\text{AP}}$ versus $[\text{Cu}(\text{acac})_2]$ was plotted to give the slopes $k_q\tau_T'$ (see Table 2 and eqn. (VI)).

3. Results

The difficulties involved in the measurement of the quantum yield of $\text{Cu}(\text{acac})_2$ photoreduction sensitized by triplet aromatic ketones have been described previously [13]. The experimental difficulties were partially overcome by the use of Ph_3P to give a clear homogeneous solution, and this allowed us to perform quantitative UV determinations [15]. Since the photodecomposition of the phenylalkyl ketones mentioned above gives AP by the type II process, the irradiation times in the presence of $\text{Cu}(\text{acac})_2$ were adjusted to give only about 5% ketone conversion, during which the

TABLE 1

Photolysis of phenylalkyl ketones in the presence of Ph_3P (0.01 M) and $\text{Cu}(\text{acac})_2$ in CH_3OH

$[\text{Cu}(\text{acac})_2] \times 10^3$ (M)	$\Phi_{\text{AP}} \times 10^2$	$\Phi_{\text{CB}} \times 10^2$	$\Phi_{\text{Cu}} \times 10^2$	$\Phi_{\text{CB}}/\Phi_{\text{AP}}$	$\Phi_{\text{AP}}/\Phi_{\text{AP}} - 1$	$1/(\Phi_{\text{AP}} + \Phi_{\text{CB}})$	α^a	$\frac{\Phi_{\text{CB}}(1 + \alpha)}{\Phi_{\text{CB}} + \Phi_{\text{AP}}}$
<i>Butyrophenone (0.2 M)^b</i>								
0.00	17.6	1.3	—	0.074	0.00	5.29	0	0.069
1.24	14.0	1.0	—	0.072	0.26	6.67	0.273	0.085
2.48	12.5	1.2	2.2	0.096	0.41	7.30	0.546	0.136
3.42	10.1	0.94	2.3	0.093	0.74	9.06	0.752	0.149
4.21	9.0	0.92	2.9	0.102	0.95	10.08	0.926	0.179
5.94	8.0	0.88	3.1	0.110	1.00	11.26	1.31	0.229
7.32	7.8	0.78	4.0	0.100	1.26	11.66	1.61	0.237
7.82	6.5	0.72	4.0	0.110	1.71	13.85	1.72	0.271
<i>Valerophenone (0.14 M)^c</i>								
0.00	61	8.6 ^d	—	0.140	0.00	1.44	0	0.123
1.23	59	8.5	—	0.144	0.033	1.48	0.251	0.158
1.84	50	7.9	—	0.158	0.22	1.72	0.188	0.206
2.45	47	7.5	—	0.160	0.30	1.83	0.500	0.213
3.07	47	7.1	1.90	0.151	0.30	1.85	0.626	0.232
3.37	49	7.8	2.14	0.159	0.25	1.76	0.688	0.315
5.40	43	7.6	2.69	0.177	0.41	1.98	1.10	0.327
5.94	42	7.3	2.68	0.174	0.44	2.03	1.21	0.375
6.78	39	7.3	3.30	0.187	0.55	2.16	1.38	0.382
7.51	36	6.5	3.90	0.178	0.67	2.33	1.53	—
<i>γ-Methylvalerophenone (0.14 M)</i>								
0.00	86	5.5	— ^e	0.064	0.00	1.09	0.00	0.060
1.2	83	5.5	—	0.066	0.04	1.13	0.233	0.091
2.4	81	5.7	—	0.070	0.06	1.15	0.466	0.096
3.4	76	6.0	—	0.079	0.13	1.22	0.660	0.122
5.4	73	6.3	—	0.086	0.18	1.26	1.05	0.163
7.5	70	6.6	—	0.094	0.23	1.31	1.46	0.212

^a $k_{\text{B}} = 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (the value for γ -methylvalerophenone) was used to calculate α for each of the three series ($\alpha = k_{\text{B}}\tau_{\text{B}}[\text{Cu}]$; see eqn. (VIII)).

^b The extent of $\text{Cu}(\text{acac})_2$ photoreduction was in the range 9% - 20%.

^c The extent of $\text{Cu}(\text{acac})_2$ photoreduction was in the range 9% - 13%.

^d Φ_{CB} of the sum for the cis isomers and trans isomers of the cyclobutanol. The two GC peaks were included for the calculations.

^e The extent of $\text{Cu}(\text{acac})_2$ photodecomposition was too small to be determined accurately.

TABLE 2

Slopes $\Sigma = k_q \tau_T'$ from the Stern–Volmer plots (eqn. (VI)): photolysis of valerophenone at a fixed concentration of Ph_3P in the presence of various concentrations of $\text{Cu}(\text{acac})_2$

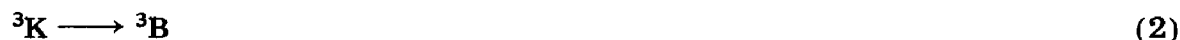
$[\text{Ph}_3\text{P}]$ (mM)	0	5	10	15	20	25
Σ (M^{-1})	112	114	83	81	62	62

concentration of $\text{Cu}(\text{acac})_2$ was reduced by 8% - 20%. The quantum yield calculations are described in this paper and also in more detail elsewhere [13, 15]. As shown in Table 1, Φ_{Cu} increased gradually on increasing the concentration of $\text{Cu}(\text{acac})_2$. In the case of γ -methylvalerophenone, the triplet state quenching was small owing to the short lifetime of the ketone triplet state ($\tau = 4.7$ ns) [16]; the decomposition of $\text{Cu}(\text{acac})_2$ was therefore too small to be accurately measured. For the photolysis of butyrophenone and valerophenone, Φ_{AP} and Φ_{CB} decreased but the latter did so only moderately. In the case of γ -methylvalerophenone, this trend was reversed; while Φ_{AP} decreased, Φ_{CB} increased slightly with increasing concentration of $\text{Cu}(\text{acac})_2$ and both changes were only moderate. In spite of the fact that the quantum yields for the three series varied in both directions, $\Phi_{\text{CB}}/\Phi_{\text{AP}}$ increased only moderately in the range of concentrations used of $\text{Cu}(\text{acac})_2$. The combined yields ($\Phi_{\text{AP}} + \Phi_{\text{CB}}$) of AP and CB are in the decreasing order: γ -methylvalerophenone > valerophenone > butyrophenone. This indicated significant triplet biradical formation in the order predicted by the reverse order of the lifetimes of the triplet excited state of these ketones (see Section 4). For comparison, the photoreduction of $\text{Cu}(\text{acac})_2$ (2.3 - 7.5 mM) sensitized by AP (0.2 M) in the presence of Ph_3P (0.01 M) was also carried out, and Φ_{Cu} varied in the range $(9.2 - 13.2) \times 10^{-3}$. These quantum yields were analysed by a steady-state treatment of the proposed mechanism. Various plots for butyrophenone photolysis are given in Figs. 1 - 4.

The photoreduction of $\text{Cu}(\text{acac})_2$ sensitized by valerophenone was examined by a similar method at various fixed concentrations of Ph_3P . The plot of Φ_{AP} versus $\text{Cu}(\text{acac})_2$ concentration for each series was analysed by using the standard Stern–Volmer equation to give the slopes Σ (which are $k_q \tau_T'$ in eqn. (VI) below) at a fixed concentration of Ph_3P (Table 2). The plot of $1/\Sigma$ against $[\text{Ph}_3\text{P}]$ is shown in Fig. 5.

4. Discussion

The mechanism for the photoreaction of phenylalkyl ketones in the presence of Ph_3P and $\text{Cu}(\text{acac})_2$ is summarized below on the basis of previous conclusions [10, 13, 15].



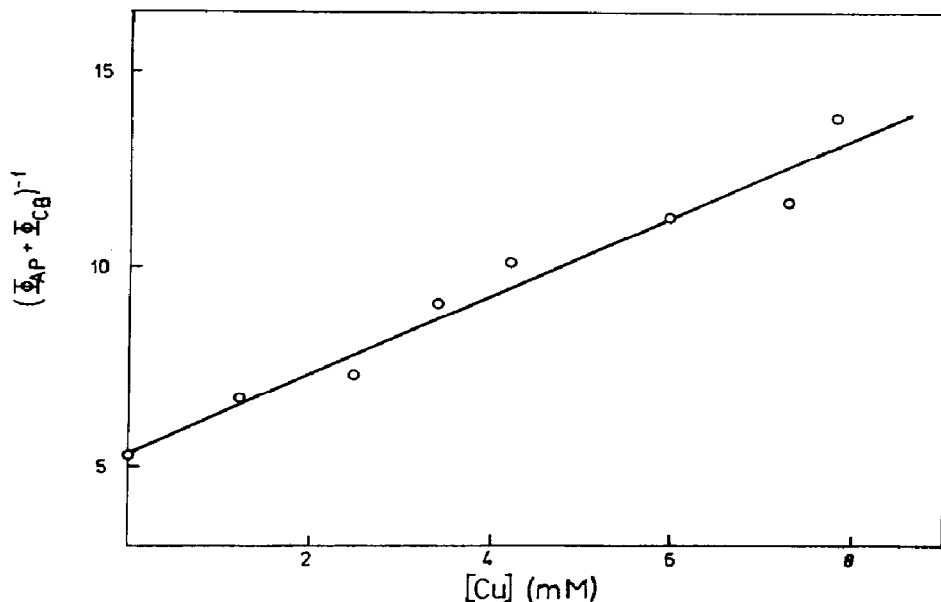


Fig. 1. Plot of $(\Phi_{AP} + \Phi_{CB})^{-1}$ vs. $[Cu]$ for the photolysis of butyrophenone (0.2 M) in the presence of $Cu(acac)_2$ in methanol containing Ph_3P (0.01 M).

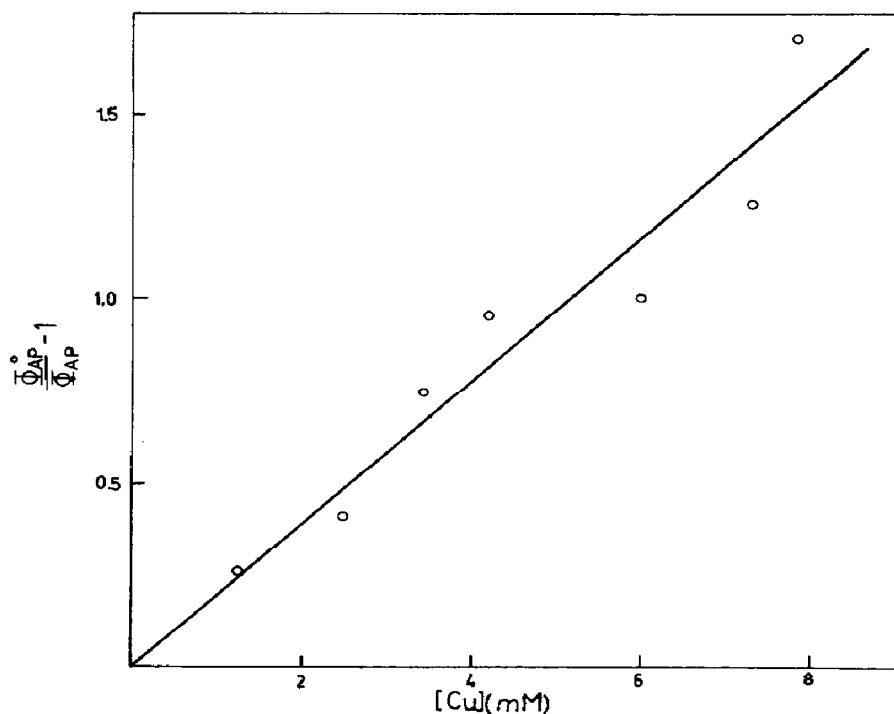
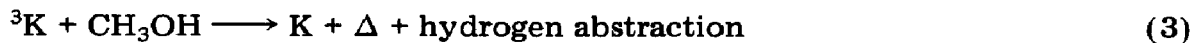


Fig. 2. Plot of $(\Phi_{AP}^0/\Phi_{AP}) - 1$ vs. $[Cu]$ for the photolysis of butyrophenone (0.2 M) in the presence of $Cu(acac)_2$ in methanol containing Ph_3P (0.01 M).



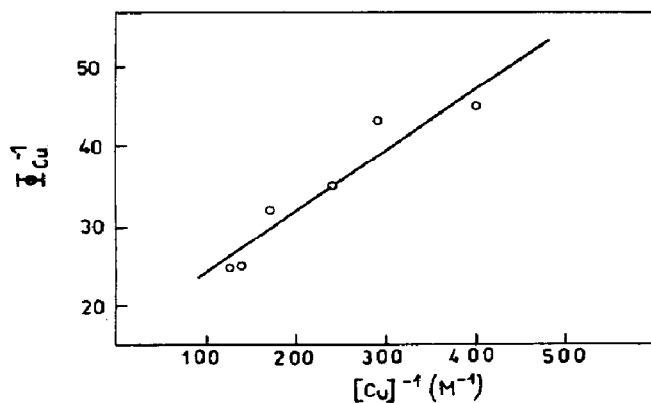


Fig. 3. Plot of Φ_{Cu}^{-1} vs. $[\text{Cu}]^{-1}$ for the photolysis of butyrophenone (0.2 M) in the presence of $\text{Cu}(\text{acac})_2$ in methanol containing Ph_3P (0.01 M).

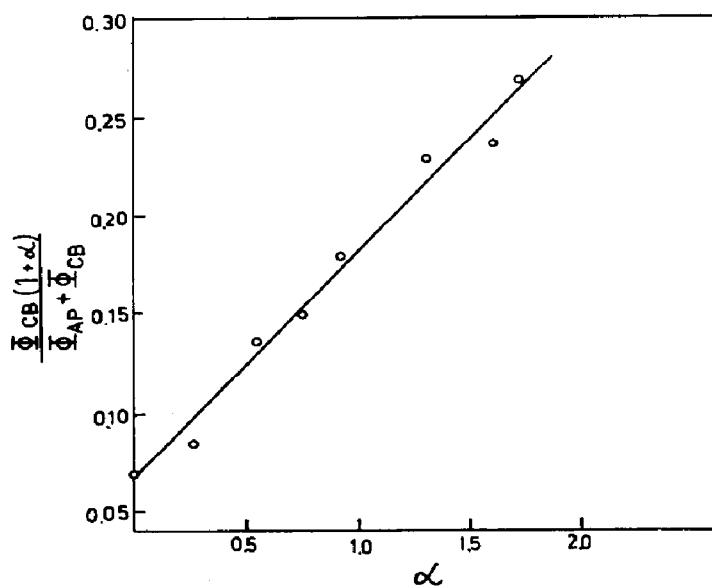
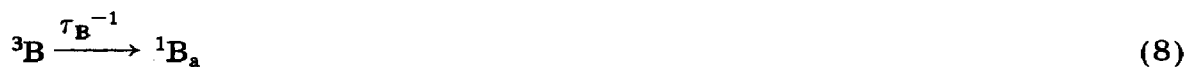
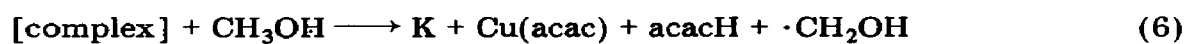


Fig. 4. Plot of $\Phi_{\text{CB}}(1 + \alpha)/(\Phi_{\text{AP}} + \Phi_{\text{CB}})$ vs. α for the photolysis of butyrophenone (0.2 M) in the presence of $\text{Cu}(\text{acac})_2$ in methanol containing Ph_3P (0.01 M).



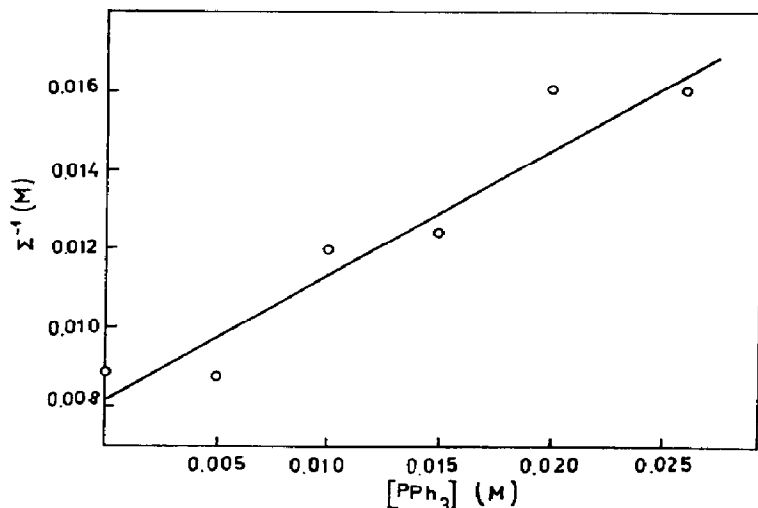


Fig. 5. Plot of Σ^{-1} vs. Ph_3P concentration for valerophenone photolysis (see Table 2 and eqn. (IX)).



Reaction (11) indicates that $\text{Cu}(\text{acac})_2$ causes catalysed ISC of the triplet radical (${}^3\text{B}$) derived from the type II reaction, without generating new products, as shown by this work and previous experiments [10]. Reactions (4) - (7) are the quenching of triplet excited state phenylalkyl ketones (${}^3\text{K}$) by Ph_3P and $\text{Cu}(\text{acac})_2$ as demonstrated previously [13, 15]. Both ${}^1\text{B}_a$ and ${}^1\text{B}_b$ are the singlet biradicals generated by intrinsic ISC and induced (by $\text{Cu}(\text{acac})_2$ in the present case) ISC respectively. These singlet radicals carry the "memory" of the conformations of the precursors [7] and this is reflected in the changing product ratios $\Phi_{\text{CB}}/\Phi_{\text{AP}}$ as the concentration of $\text{Cu}(\text{acac})_2$ increases.

The variations in the quantum yields are analysed on the basis of a steady state for the mechanism proposed in reactions (1) - (13). The following kinetic equations can be derived from the definition of the quantum yields, where $[\text{Cu}]$ is the concentration of $\text{Cu}(\text{acac})_2$.

$$\Phi_{\text{AP}} = \frac{k_2}{(k_2 + k_3 + k_4[\text{Ph}_3\text{P}] + k_q[\text{Cu}])(k_8 + k_{\text{B}}[\text{Cu}])} \left(\frac{k_{12}k_{\text{B}}[\text{Cu}]}{k_{12} + k_{13}} + \frac{k_8k_9}{k_9 + k_{10}} \right) \quad (I)$$

$$\Phi_{\text{CB}} = \frac{k_2}{(k_2 + k_3 + k_4[\text{Ph}_3\text{P}] + k_q[\text{Cu}])(k_8 + k_{\text{B}}[\text{Cu}])} \left(\frac{k_{13}k_{\text{B}}[\text{Cu}]}{k_{12} + k_{13}} + \frac{k_8k_{10}}{k_9 + k_{10}} \right) \quad (II)$$

$$\frac{1}{\Phi_{\text{AP}} + \Phi_{\text{CB}}} = \frac{1}{k_2\tau_{\text{T}'}} + \frac{k_q[\text{Cu}]}{k_2} \quad (III)$$

where

$$\tau_T' = (k_2 + k_3 + k_4[\text{Ph}_3\text{P}])^{-1} \quad (\text{IV})$$

From eqn. (I)

$$\frac{\Phi_{\text{AP}}^\circ}{\Phi_{\text{AP}}} = \frac{1 + k_q\tau_T'[\text{Cu}]}{\Phi_{\text{B}}(b/a - 1) + 1} \quad (\text{V})$$

where

$$\Phi_{\text{B}} = k_{\text{B}}[\text{Cu}](k_8 + k_{\text{B}}[\text{Cu}])^{-1}$$

$$a = k_9(k_9 + k_{10})^{-1}$$

and

$$b = k_{12}(k_{12} + k_{13})^{-1}$$

When a and b are approximately equal (*i.e.* when the presence of $\text{Cu}(\text{acac})_2$ does not alter $\Phi_{\text{CB}}/\Phi_{\text{AP}}$ drastically; such a situation indeed exists as shown in Table 3), eqn. (V) reduces to the standard Stern–Volmer equation

$$\frac{\Phi_{\text{AP}}^\circ}{\Phi_{\text{AP}}} = 1 + k_q\tau_T'[\text{Cu}] \quad (\text{VI})$$

Alternatively, k_q can be related to Φ_{Cu} by a modified Stern–Volmer equation:

$$\frac{1}{\Phi_{\text{Cu}}} = \frac{1}{\beta} + \frac{1}{\beta k_q\tau_T'[\text{Cu}]} \quad (\text{VII})$$

where $\beta = k_6(k_6 + k_7)^{-1}$. This equation is obtained by assuming that the interaction of $\text{Cu}(\text{acac})_2$ with ^3B (reaction (11)) does not cause photoreduction of the $\text{Cu}(\text{acac})_2$, and this is supported by the analysis below.

From eqns. (I) and (II), the dependence of the formation of CB on $\text{Cu}(\text{acac})_2$ concentration can be related to the mechanism. It should be noted that the ratio of Φ_{CB} to $(\Phi_{\text{AP}} + \Phi_{\text{CB}})$ is independent of k_q , *i.e.* it is not related to the quenching of the triplet excited state by $\text{Cu}(\text{acac})_2$ in reaction (5).

$$\frac{\Phi_{\text{CB}}(1 + \alpha)}{\Phi_{\text{AP}} + \Phi_{\text{CB}}} = \frac{k_{10}}{k_9 + k_{10}} + \frac{\alpha k_{13}}{k_{12} + k_{13}} \quad (\text{VIII})$$

where $\alpha = k_{\text{B}}\tau_{\text{B}}[\text{Cu}]$.

$k_q\tau_T'$ is obtained from the plots of eqns. (III), (IV) and (VII) (Figs. 1–3) by using the experimental quantum yields Φ_{AP} , Φ_{CB} and Φ_{Cu} . As shown in Table 3, the agreement is good in spite of the fact that quantum yields from different sources are utilized in the computation. The agreement confirms that the approximation $a = b$ in eqn. (V) is valid, and that the quenching of triplet state ketones by $\text{Cu}(\text{acac})_2$ is not related to variations in Φ_{AP} and

TABLE 3
Summary of the kinetic data

Ketone	$k_q \tau_T' (M^{-1})$		τ_T^a (ns)	τ_T^{b} (ns)	$k_q \times 10^{-9} (M^{-1} s^{-1})$		τ_B^c (ns)	$k_{10}/(k_9 + k_{10}) k_{13}/(k_{12} + k_{13})$ (eqn. (VIII)) (eqn. (VIII))			
	Equa- tion (III)	Equa- tion (VI)			Equa- tion (VII)	Equa- tion (III)			Equa- tion (VI)	Equa- tion (VII)	
PhCOCH ₂ CH ₂ - CH ₃	187 ± 20	195 ± 11	218 ± 75	70	35	5.4	5.6	6.2	110	0.065 ± 0.007	0.117 ± 0.007
PhCOCH ₂ CH ₂ - CH ₂ CH ₃	74 ± 8	83 ± 5	91 ± 26	16	12.3	6.0	6.7	7.4	102	0.116 ± 0.005	0.178 ± 0.006
PhCOCH ₂ CH ₂ - CH(CH ₃) ₂	28 ± 3	32 ± 2	—	4.7	4.3	6.5	7.4	—	97	0.058 ± 0.006	0.102 ± 0.007
PhCOCH ₃	—	—	511 ± 53	200	67	—	—	7.6	—	—	—

^a τ_T is cited from ref. 16.

^b τ_T' was calculated from eqn. (IV) using $[Ph_3P] = 0.01$ M and a value of k_4 from ref. 15.

^c τ_B is cited from ref. 16.

Φ_{CB} . The rate constants k_q for triplet quenching by $\text{Cu}(\text{acac})_2$ are about $6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for all phenylalkyl ketones studied, including AP, as shown in Table 3. These agree well with that for propiophenone ($k_q = 7.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) determined from laser flash photolysis [13].

In eqn. (V), the numerator represents triplet excited state quenching, and biradical quenching is represented by the denominator $\Phi_B(b/a - 1) + 1$ which is calculated to vary in the range 1.00 - 0.96 from the data obtained previously [10] and for the $\text{Cu}(\text{acac})_2$ concentrations of 10^{-2} - 10^{-3} M used in this work. It follows that in the quenching of the Norrish type II photo-reaction by $\text{Cu}(\text{acac})_2$, the magnitude of Φ_{AP} is primarily determined by the extent of the triplet excited state reactions and only very slightly by the biradical quenching process. This is supported by the fact that the experimental Φ_{AP} in the three series increase as the triplet excited state lifetimes τ_T of the phenylalkyl ketones decrease (see Table 1). It should be noted that the triplet radical lifetimes τ_B of the three ketones are similar and therefore would not generate such differences in Φ_{AP} .

A quantitative evaluation of the effects of $\text{Cu}(\text{acac})_2$ on the formation of CB can be obtained from the plots (Fig. 4) of eqn. (VIII), in which k_B is assumed to be $2.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (the rate constant of reaction (11) for the triplet biradical derived from γ -methylvalerophenone obtained from flash photolysis [10]), for those derived from the two other phenylalkyl ketones in the calculation of α (Table 1). As the nature of the interaction is the same for all three cases, this assumption would not be expected to cause big errors. Indeed, there is good evidence that, under comparable conditions, the interactions of a triplet biradical with similar substrates (therefore producing the same type of products) give similar rate constants [3]. From these plots, the rate $k_{10}(k_9 + k_{10})^{-1}$ of formation of CB from intrinsic ISC and the rate $k_{13}(k_{12} + k_{13})^{-1}$ from induced ISC can be obtained from the intercepts and slopes (Table 3). These values for γ -methylvalerophenone are the same within experimental error as those obtained from the experiments [10] without Ph_3P . The values for butyrophenone and valerophenone may not be precise but they would not be expected to deviate significantly from those shown. Undoubtedly, they show that $\text{Cu}(\text{acac})_2$ interacts with a triplet biradical and this favours the formation of CB rather than AP. Since it is known that the singlet radicals $^1\text{B}_a$ and $^1\text{B}_b$ carry the memory of the conformation of their precursors, it is logical to assume that some kind of coordination between the phenylalkyl ketones and the copper atom is carried over to the biradical stage. However, these values do not show a sufficiently clear trend to be able to correlate them with the increasing crowding of the side chain.

The results of the static quenching experiments described in this paper appear to be complex and to require an elaborate mechanism for their interpretation. It is desirable to check the kinetic scheme with some known data. In particular, any possible hidden interactions of Ph_3P with reactive intermediates should be examined. From eqn. (VI) it is seen that $k_q\tau_T' = \Sigma$ is obtained at different concentrations of Ph_3P (Table 2). From eqn. (IV), Σ

can be expressed by

$$\frac{1}{\Sigma} = \frac{1}{k_q\tau_T} + \frac{k_4[\text{Ph}_3\text{P}]}{k_q} \quad (\text{IX})$$

where $\tau_T = (k_2 + k_3)^{-1}$.

The plot from the results for valerophenone photolysis is shown in Fig. 5; $k_4\tau_T = \text{slope/intercept}$ is determined to be $40 \pm 7 \text{ M}^{-1}$. The rate constant k_4 for the quenching of triplet state valerophenone ($\tau_T = 16 \text{ ns}$ [16]) by Ph_3P is calculated to be $2.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, which agrees with the value $1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ obtained from direct quenching experiments [15]. Taking $k_4 = 1.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, the rate constant for the quenching of triplet excited state valerophenone by $\text{Cu}(\text{acac})_2$ can be calculated from the slope (0.33) as $5.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The agreement with that shown in Table 3 is excellent. It is also noted that $(k_q\tau_T)^{-1}$ calculated from Table 3 agrees reasonably well with the intercept (0.0082) in Fig. 5. In previous studies [13], we were uncertain whether it was possible for an interaction to occur between Ph_3P and the complex in reaction (5). The agreement shown above leaves no doubt that Ph_3P does not interact with such a complex to change the reaction pattern of the aromatic-ketone-sensitized photoreduction of $\text{Cu}(\text{acac})_2$.

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