Benzene-sensitized Photoreduction of Bis(acetylacetonato)copper(II) under Hydrogen

Yuan L. Chow,* Gonzalo E. Buono-Core, Bronislaw Marciniak, and Huali Li
Department of Chemistry, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

New sets of conditions for sensitized photoreduction of $Cu(acac)_2$ to copper(I) complexes have been discovered. It was demonstrated that singlet excited-state benzene could sensitize the photoreduction just as well as triplet state benzophenone and hydrogen could act as a hydrogen-atom donor. E.s.r. spectroscopy was used to monitor the efficiency of these photoreductions. Better photoreduction efficiency at a higher pressure of hydrogen as well as deuterium incorporation is clear evidence that hydrogen-atom transfer is the rate-regulating step in the photoreduction. The quantum yield determination of $Cu(acac)_2$ photoreduction and benzene fluorescence quenching showed that singlet excited-state benzene was quenched by $Cu(acac)_2$ with a rate constant, k_q, of 3.6—5.5 × 10^9 l mol^{-1} s^{-1}. The quenching interaction is assumed to occur by energy-transfer mechanism.

Ketones with high triplet energies ($E_T > 69$ kcal mol^{-1}) promote the photoreduction of $Cu(acac)_2$ *via* charge transfer (CT) complexes [equation (1)] to give Cu(acac), a Cu^I complex, as a black precipitate.[1–3] As the quantum yields of $Cu(acac)_2$ disappearance increase in the same order of hydrogen-atom-donating abilities of solvent SH, hydrogen-atom transfer to the CT complex is proposed as the rate-regulating step [equation (2)] which competes against the reversion of the complex to the ground-state components[3,4] [equation (3)]. While direct photolysis by the excitation of the charge transfer to metal (CTTM) transition at 230—250 nm of $Cu(acac)_2$ also gives the same product pattern, irradiation of the absorption >290 nm (Pyrex filter) causes no reaction.[1–3,5] Aside from the preparative point of view,[2] the sensitized photoreduction poses intriguing mechanistic questions about the nature of the complex, hydrogen abstraction, and electron transfer *versus* spin exchange.[3,4] We have discovered that singlet excited-state benzene can sensitize the photoreduction and that hydrogen can act as a hydrogen-atom donor: the results are reported here.

$$^{*}R_2C{=}O + Cu(acac)_2 \longrightarrow [R_2C{=}O^{-\bullet} --- Cu(acac)^+ --- acac^{\bullet}] \quad (1)$$

$$[Complex] + S{-}H \longrightarrow R_2C{=}O + Cu(acac) + acacH + S^{\bullet} \quad (2)$$

$$[Complex] \longrightarrow R_2C{=}O + Cu(acac)_2 \quad (3)$$

$$Cu(acac) + 2L \longrightarrow Cu(acac)L_2 \quad (4)$$

Experimental

Equipment and Materials.—The same equipment and materials as described previously[3,6] were used. Benzophenone-sensitized experiments were irradiated through a Pyrex filter whereas benzene-sensitized ones were through a Corex filter, using a 450 W medium-pressure Hanovia mercury lamp unless specified otherwise. A Perkin-Elmer MPF 44-B fluorescence spectrophotometer was used. E.s.r. spectroscopy was carried out with a Varian E-4 spectrometer (X-band, 9 GHz) equipped with a Varian E-257/WL-257 variable-temperature accessory. A Varian Strong Pitch sample (*g* 2.0026) was used as the external standard. Nitrogen and hydrogen gas (Union Carbide) were purified by scrubbing through a Fieser solution followed by concentrated H_2SO_4 and then KOH pellets. Deuterium gas (Canadian Liquid Air, C.P.) was passed through molecular sieves 3A before introduced into the reaction vessel.

Photolysis of $Cu(acac)_2$ *under Nitrogen.*—(1) *In toluene.* A suspension of $Cu(acac)_2$ (0.14 g, 0.55 mmol) and benzophenone (0.364 g, 2.0 mmol) in toluene (110 ml) under nitrogen was irradiated through a Pyrex filter. A dark yellow solution was obtained in 20 min and, in 30 min, a black colloidal suspension appeared. The sample filtered through a silica column gave the peaks for bibenzyl (16% at 6.90 min) and benzophenone (98% at 7.99 min). The peaks were identified by coinjections of authentic samples. In 1 h of irradiation, heavy black precipitates were formed and bibenzyl increased to 47%. After 2.5 h of irradiation, the black precipitate disappeared to give metallic copper deposited on the vessel.

A similar solution irradiated for 1.5 h was treated with Ph_3P (0.30 g, 1.15 mmol). The black precipitates disappeared after stirring for 2 h under N_2. The solvent was evaporated and the residue was washed with ether to give a solid (0.294 g) which was recrystallized from benzene–ether to give $Cu(acac)(Ph_3P)_2$, m.p. 178—180 °C; the i.r. spectrum was superimposable with that of the authentic sample.[1,2]

(2) *In benzene.* A similar suspension of $Cu(acac)_2$ and benzophenone in benzene (110 ml) was irradiated through a Pyrex filter for 8 h without appreciable change in the colour. G.c. analysis of photolysate showed only the benzophenone peak (7.9 min) in a quantitative recovery. $Cu(acac)_2$ was recovered in 95% yield.

Photolysis of $Cu(acac)_2$ *in Benzene under Hydrogen.*—(1) *Benzophenone-sensitized reactions.* A solution of $Cu(acac)_2$ (0.5 g, 1.92 mmol) and benzophenone (1.0 g, 5.5 mmol) in benzene (200 ml) was irradiated through a Pyrex filter under hydrogen with a 450 W lamp to give, in 20 min, a cloudy yellow solution which turned to blue on exposure to air. Prolonged irradiation deposited yellow film on the wall but no copper metal. G.c. analysis gave only the benzophenone peak at 7.85 min.

A similar solution irradiated with a 200 W lamp for 5 h turned to a cloudy yellow solution. To this Ph_3P (1 g) was added under nitrogen to give a clear solution. The residue was recrystallized from benzene–ether to afford $Cu(acac)(Ph_3P)_2$ (1.2 g), m.p. 176—180 °C.[1,2]

(2) *Benzene sensitization.* A solution of $Cu(acac)_2$ (0.15 g, 0.58 mmol) in benzene (80 ml) was irradiated through a Corex filter under hydrogen for 2 h to give a dark yellow solution. A degassed benzene solution (30 ml) of Ph_3P (0.30 g, 1.15 mmol)

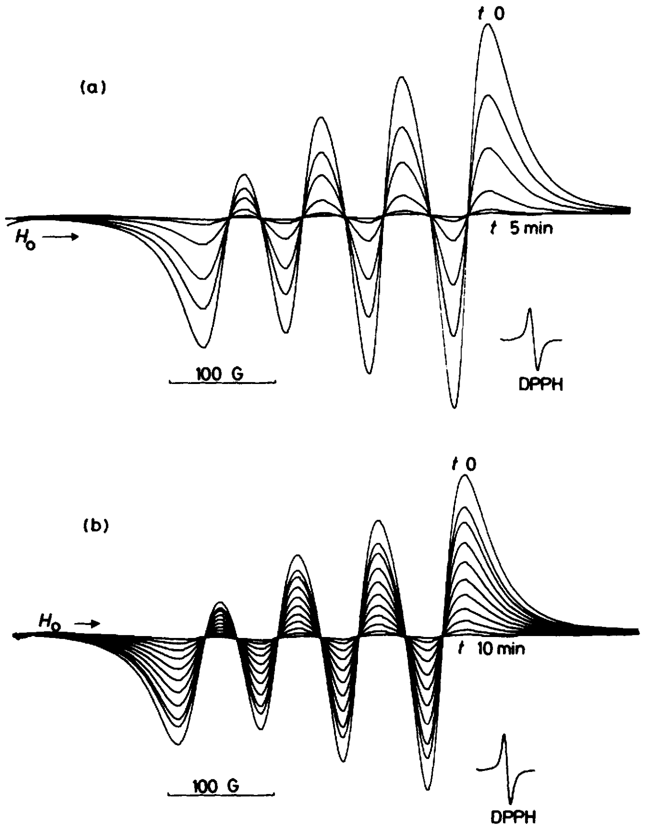


Figure 1. E.s.r. traces during irradiation (Pyrex filter) of Cu(acac)$_2$–benzophenone (0.01M) in toluene under nitrogen: consecutive scannings were made at 1 min intervals: (a) Cu(acac)$_2$ 0.001M; (b) Cu(acac)$_2$ 5 × 10^{-4}M and P(OEt)$_3$ 1 × 10^{-3}M

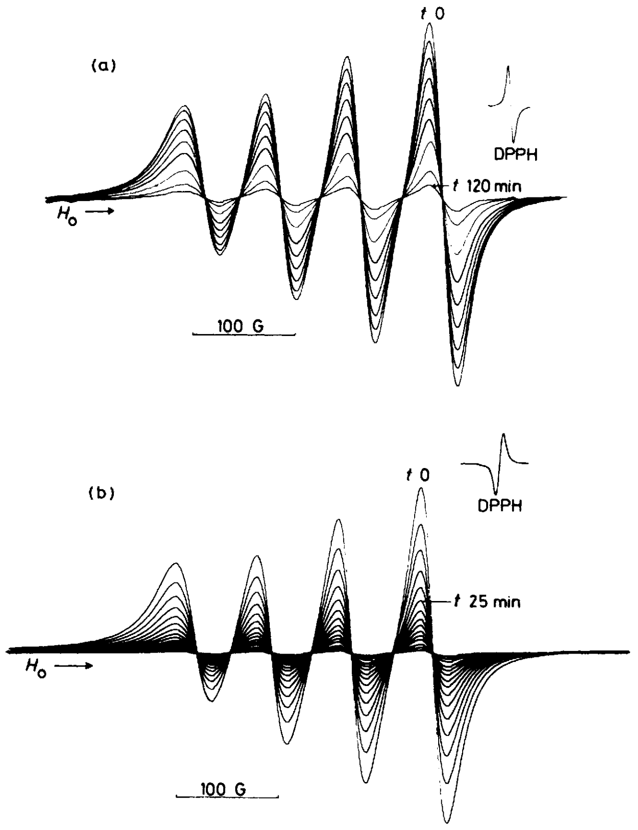


Figure 2. E.s.r. traces during irradiation of Cu(acac)$_2$ in benzene saturated with hydrogen: (a) Cu(acac)$_2$ 8.5 × 10^{-4}M, Corex filter, consecutive scannings at 15 min intervals; (b) Cu(acac)$_2$ 0.001M–benzophenone 0.05M, Pyrex filter, consecutive scannings at 5 min intervals

was added and the mixture was stirred for 2 h to give a solution. The residue was treated with ether (25 ml) to give crude Cu(acac)(Ph$_3$P)$_2$ as a powder (0.3 g) which was recrystallized from benzene–ether to afford a sample showing an identical i.r. spectrum to that of Cu(acac)(Ph$_3$P)$_2$.

A photolysate obtained in the same way was filtered through a silica column. The residue obtained after vacuum evaporation was analysed by g.c. to give peaks at 0.72 min for acetylacetone and 1.90 and 1.95 min (1:1 ratio) for *cis*- and *trans*-acetylacetone enol acetate that showed the M^+ peak (by chemical ionization) 143 (65%) and 101 (100). By electron-impact mass spectra, the former showed *m*/*e* 142 (< 1%), 100 (63), 85 (90), and 43 (100) and the latter 142 (< 1%), 100 (82), 85 (100), and 43 (73). The two acetates were isolated by preparative g.c. as a mixture; δ(CDCl$_3$) 2.163 (s, 3 H), 2.197 (s, 1.6 H), 2.231 (s, 3 H), 2.294 (d, *J* 1.2 Hz, 1.4 H), 5.857 (s, 0.55 H), and 6.070 (br q, 0.45 H); $\nu_{max.}$ 1 770 (s), 1 707 (s), 1 670 (s), 1 635 (s, br), 1 435 (m), 1 375 (s), 1 200—1 140 (br), and 1 030 (s) cm^{-1}.

A solution of Cu(acac)$_2$ (0.4 g) and tri-n-butylphosphine (0.8 g) in benzene (200 ml) was irradiated for 1 h. Benzene was removed under reduced pressure to give a brown semi-solid. The solid was treated with ether under nitrogen and precipitated Cu(acac)$_2$ was removed. The solution was evaporated to give a brown oil of Cu(acac)(PBu$^n{}_3$)$_2$ (0.48 g, 60%), $\nu_{max.}$(neat) 2 961 (s), 2 930 (s), 2 570 (s), 1 610 (s), 1 510 (m), 1 465 (m), 1 382 (m), 1 152 (m), 1 097 (w), and 913 (w) cm^{-1}. A CH$_2$Cl$_2$ solution of the oil was slowly oxidized by the air to a blue solution. Owing to air oxidation the n.m.r. spectrum taken under N$_2$ showed broad signals at δ 1.8, 5.1, and 0.8—1.5.

A benzene solution (5 ml) of Cu(acac)$_2$ (5.75 × 10^{-3}M) and hex-1-yne (1.15 × 10^{-2}M) in a quartz tube was saturated with hydrogen and sealed. This solution was irradiated through a Corex filter to give a dark yellow solution which was evaporated to afford CuC≡C(CH$_2$)$_3$CH$_3$; identical i.r. spectrum (1 927 cm^{-1}) with that of an authentic sample.^{2} CH$_3$(CH$_2$)$_3$C≡CCu(Ph$_3$P)$_2$ was formed on treatment with Ph$_3$P and was recrystallized from acetonitrile, m.p. 155 °C (decomp.).^{2}

E.s.r. Experiments.—A solution of Cu(acac)$_2$ (0.001M) and benzophenone (0.05M) in toluene was prepared. This solution (150 μl; 18 mm height) was placed into a quartz sample tube (i.d. 3 mm and o.d. 4 mm) and capped with a rubber septum. The solution was purged with nitrogen or argon for 10 min and placed in the e.s.r. cavity; the cavity has a 14 mm opening for irradiation. The light source was a 200 W high-pressure PEK 212 lamp filtered through CoSO$_4$ solution (24 g l^{-1}; 5 cm) and a Pyrex filter (1.9 mm); this supplied light source at 300—400 mm; the intensity was further attenuated with an i.r. attenuator. The light was placed *ca.* 50 cm from the cavity. The Cu(acac)$_2$ signals were recorded at regular intervals while the solution was irradiated continuously (Figure 1). The plots of the intensities of the highest peaks *versus.* time gave zero-order kinetics. The initial 10—18% decreases of the height were used to calculate quantum yields; the average of 26 determinations was 0.052 ± 0.002. In methanol, ethanol, and propan-2-ol solution similar experiments gave similar e.s.r. spectra; the zero-order plots showed some curvature and reproducibility was poor.

Photolysis of benzene solution of Cu(acac)$_2$ (0.001M) and benzophenone (0.05M) was carried out after the solution was

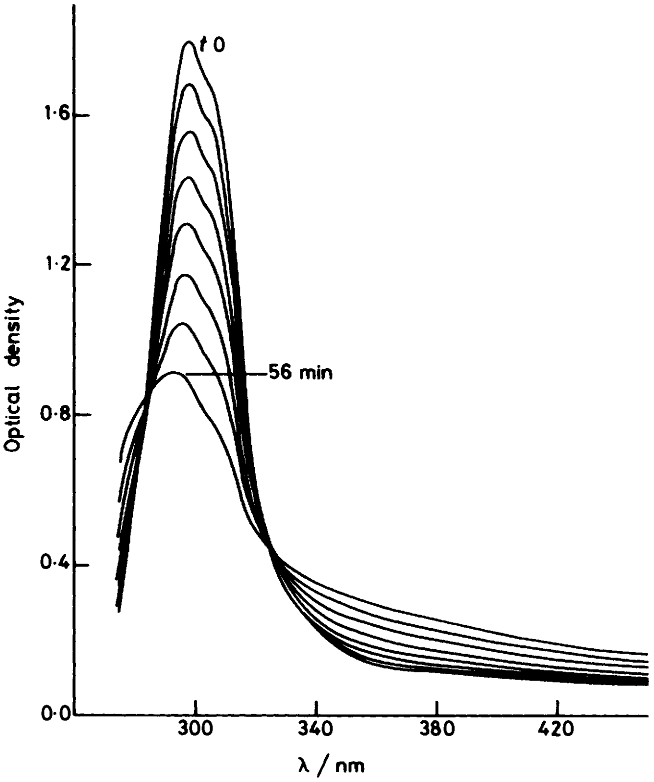


Figure 3. Irradiation of $Cu(acac)_2$ 8×10^{-5}M in benzene under hydrogen through a Corex filter: the curves were recorded at 8 min intervals

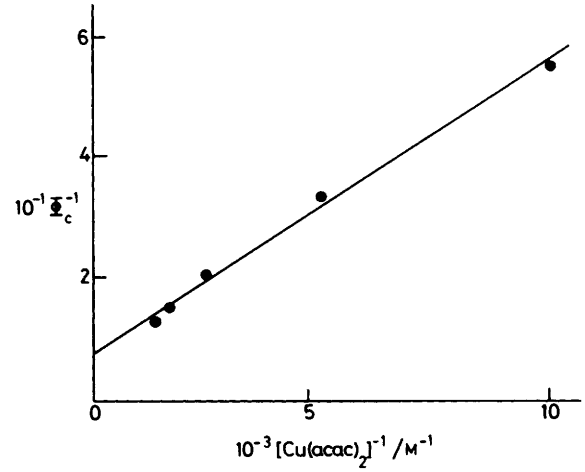


Figure 4. Plot of $1/\Phi_c$ *vs.* $(1/[Cu(acac)_2]$

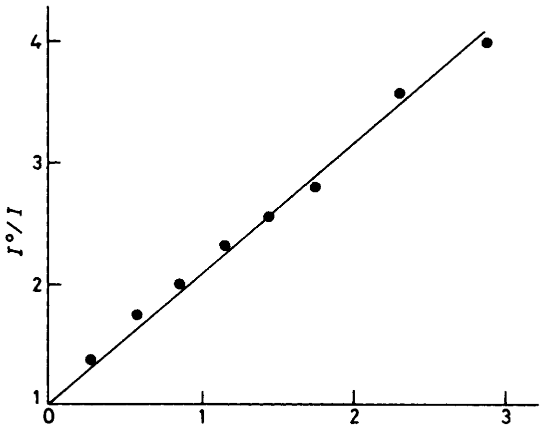


Figure 5. Stern–Volmer plot of benzene fluorescence quenching by $Cu(acac)_2$

saturated with hydrogen at 2, 4, and 8 lb in^{-2} above atmospheric pressure and sealed under a septum cap. The spectra were recorded every 5 min (Figure 2b). The heights of the highest signal were expressed in terms of % of the zero-time height and the percentage heights were plotted against time. The decreases of % heights in 5 min were 21 ± 2, 16 ± 2.5, and 10 ± 2 for the experiments at 8, 4, and 2 lb in^{-2}, respectively: the errors were calculated from 5—8 experiments in each series.

A solution of benzophenone (0.05M) and diphenylmethanol (0.1M) in benzene (Φ 0.74) was used as the secondary actinometer.[7] The solution (150 μl) placed in an e.s.r. tube was irradiated with the same light source. The solution was diluted with benzene (200 μl) and the optical density at 360 nm was examined by u.v. spectroscopy.

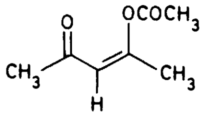
A benzene solution of $Cu(acac)_2$ (8.5×10^{-4}M) under hydrogen was irradiated as above through a Corex filter and the e.s.r. spectra were taken at 15 min intervals (Figure 2a).

Photolysis of $Cu(acac)_2$ *in Benzene under Deuterium.*—A suspension of $Cu(acac)_2$ (100 mg) in dry benzene in a quartz tube was irradiated through a Corex filter under deuterium for 3 h, when the solution turned to yellow. Benzene was removed under vacuum and a few drops of dry CH_2Cl_2 were added to the residue. Filtration gave a green solution. G.c.—m.s. (60° isothermal) gave the acetylacetone peak at 1.89 min: *m/e* 101 (22.4%), 100 (54), 85 (100), and 43 (84). Monodeuterioacetylacetone was calculated on the *m/e* 100—101 peak to be 26%.

Absorption and Fluorescence Spectroscopy.—Absorption spectra were recorded with a Cary 210 spectrophotometer using u.v. cells of 0.001—1.000 cm path lengths. Fluorescence quenching experiments were carried out using a 'front face' viewing technique.[8–10] For this purpose, the spectrofluorimeter sample holder was modified to accommodate a 0.1 cm cell. Benzene solutions of $Cu(acac)_2$ ($0 \approx 2.9 \times 10^3$M) were deoxygenated with argon or hydrogen and excited at 265 nm. At these concentrations, benzene absorbed >98% of the incident light and exhibited the fluorescence emission as published before.[10] The decreases of emission intensities were monitored at 285, 294, and 306 nm. The variations of I/I_0 values of three readings at a fixed concentration were within ±1% and the average values of these I/I_0 were used for the Stern–Volmer plot (Figure 4).

Kinetics Measurements.—A solution of $Cu(acac)_2$ (8.0×10^{-5}M) in benzene in a u.v. cell (1 cm) was saturated with hydrogen and sealed under a septum cap. While the solution was irradiated with a PEK 212 lamp through a Corex filter, u.v. traces were recorded in the 270—450 range (Figure 3). The plot of o.d. at 298 nm gave a straight line.

Irradiation for the determination of the Stern–Volmer relation was carried out as above with benzene solutions of $Cu(acac)_2$ (8×10^{-4}—8×10^{-5}M) saturated with hydrogen in a 0.1 cm cell. Irradiation time was adjusted to cause 5—10% conversion of $Cu(acac)_2$ (Figure 5).



(1)

Results and Discussion

Irradiation of benzophenone and Cu(acac)$_2$ in toluene through a Pyrex filter quickly gave a dark yellow solution which started to deposit black precipitates of Cu(acac) polymers and eventually metallic copper on further irradiation; toluene served as a hydrogen-atom donor and was oxidized to bibenzyl. While the similar benzophenone-sensitized (Pyrex filter) photolysis in benzene solution *under nitrogen* did not cause any changes, *under hydrogen* the blue solution was rapidly photoreduced to a yellow solution which slowly deposited an amorphous yellow coating on the reaction vessel, retarding light passage. The unknown yellow products were shown to be Cu(acac) derivatives by the reaction with phosphines that led to the formation of Cu(acac)(Ph$_3$P)$_2$ and Cu(acac)[PBu$^n{}_3$]$_2$. Control experiments showed that benzophenone was not reduced when photolysed in benzene *under hydrogen.*

In the absence of benzophenone, Cu(acac)$_2$ in benzene was irradiated under hydrogen through a Corex filter (>260 nm) to give a similar yellow solution and precipitates of Cu(acac) derivatives which could not be purified. The addition of Ph$_3$P or PBu$^n{}_3$ gave the phosphine complexes of Cu(acac). From the photolysate, in addition to acetylacetone, the *cis-* and *trans-*isomers of acetylacetone enol acetate (1) were isolated as a mixture. I.r. absorptions at 1 707 and 1 770 cm^{-1} confirmed the enol acetate linkage. *cis–trans*-Geometry could not be assigned to the two compounds but the n.m.r. and mass spectra clearly indicated they are geometrical isomers. Phosphine complexes of Cu(acac) were also obtained in the irradiation of Cu(acac)$_2$ in the presence of phosphines in the benzene–hydrogen system. Likewise, photolysis in the presence of hex-1-yne gave the corresponding copper(I) acetylide. These experiments establish that benzene can sensitize the photoreduction and hydrogen can act as a hydrogen-atom donor.

As copper(II) complexes have a d^9 configuration and copper has a nuclear spin number of 3/2, Cu(acac)$_2$ shows a four-line e.s.r. signal[11] as in Figure 1. The intensities of the signals decreased regularly as a toluene solution containing Cu(acac)$_2$ and benzophenone under nitrogen was irradiated in the cavity through a Pyrex filter (Figure 1a). The plots of the highest peak intensities in each spectra gave good zero-order correlations. Since all the signals passed through isosbestic points, the heights of the signals were proportional to the concentration of Cu(acac)$_2$. For the photoreduction of Cu(acac)$_2$ in toluene, the quantum yields were determined using benzophenone–diphenylmethanol[7] as the actinometer to be 0.052 ± 0.002. In the presence of P(OEt)$_3$, the disappearance of the e.s.r. signals (Figure 1b) coincided with the fading of the blue colour of Cu(acac)$_2$; the solution was slowly oxidized on exposure to the air and restored the original four-line signal. The quantum yield determination in alcohols gave large errors that may arise from the rapid formation of black precipitates and metallic copper.

In the benzene–nitrogen system, the e.s.r. signal did not decrease whether sensitized by benzophenone (Pyrex filter) or benzene (Corex filter). In the benzene–hydrogen system, the photoreduction of Cu(acac)$_2$ by either sensitization was facile and could be monitored by e.s.r. spectroscopy (Figure 2). The solubility of hydrogen in benzene[12] is 2.75×10^{-3}M at 23 °C which limits the usable Cu(acac)$_2$ concentration range in sealed-tube experiments. The rate of the disappearance gave poor reproducibility in a sealed tube under hydrogen pressure. However, the relative rates of the decreases of the e.s.r. peak were faster at higher pressure, *e.g.* 2.1 : 1.6 : 1 under 8, 4, and 2 lb in^{-2} hydrogen pressures, respectively. The observations indicate that hydrogen-atom transfer from hydrogen to the complex [*e.g.* equation (2)] is the rate-determining step. The confirmatory evidence for the participation of hydrogen was gained by photolysis of Cu(acac)$_2$ in benzene in the presence of deuterium from which monodeuteriated acetylacetone was obtained in a 26% yield.

For 10^{-4}—10^{-5}M-Cu(acac)$_2$, the progress of the benzene sensitized photoreduction (Corex filter) could be followed as shown in Figure 3; the decreases of the 293—298 nm peak of Cu(acac)$_2$ were replaced by a new, weaker peak at *ca.* 350 nm with isosbestic points at 284 and 325 nm. A control experiment using Cu(acac)$_2$ in methanol under the same irradiation conditions showed no change in the 293—298 nm peak. The plot of optical density at 295 nm *versus* irradiation times gave an excellent zero-order plot indicating that the reduction of Cu(acac)$_2$ to a Cu^I complex was indeed induced by photoexcitation of benzene. Because of the precipitation problem, a high concentration could not be used and the identity of the new peak at 350 nm could not be elaborated. Undoubtedly, this peak arises from the yellow Cu(acac) complex which may be a loose Cu(acac)–benzene complex.

In order to gain insight into the interaction of excited-state benzene and Cu(acac)$_2$, the quenching of photoreduction as well as benzene fluorescence was investigated. The quantum yield of the benzene-sensitized photoreduction of Cu(acac)$_2$ (*ca.* 10^{-3}—10^{-5}M) was monitored by u.v. spectroscopy as shown above. The quantum yields of Cu(acac)$_2$ disappearance (Φ_c) is related to Cu(acac)$_2$ concentrations by equation (5) where k_q is

$$1/\Phi_c = 1/\beta + 1/\{\beta k_q \tau_o[\mathrm{Cu(acac)_2}]\} \qquad (5)$$

the rate constant of the quenching step, τ_o the singlet excited state lifetime of benzene, and $\beta = k_8/(k_8 + k_9)$ the partition coefficient of the complex to two competing reactions. A plot of $1/\Phi_c$ *versus* $1/[\mathrm{Cu(acac)_2}]$ (Figure 4) gave a straight line (r 0.9914) from which $k_q\tau_o$ (= intercept/slope) is calculated to be $1\,660 \pm 300$ l mol^{-1}.

Neat benzene exhibits fluorescence emission of both monomer and excimer[10] that is in a rapid equilibrium at room temperature. Because of the rapid reversibility, quenching of benzene fluorescence by Cu(acac)$_2$ can be examined on the intensity reduction of either species, *e.g.* either benzene or excimer fluorescence. Owing to the emission peak of benzene overlapping with absorption of Cu(acac)$_2$, the fluorescence quenching by a conventional technique shows a complex pattern arising from trivial quenching. This can be avoided[8,13] by the 'front view technique' and the regular Stern–Volmer equation (6) can be used where I and I^o are the benzene

$$I^o/I = 1 + k_q\tau_o[\mathrm{Cu(acac)_2}] \qquad (6)$$

fluorescence intensities at fixed wavelength in the presence and the absence of [Cu(acac)$_2$] and $k_q\tau_o$ the same meaning as equation (5). The plot of I^o/I *versus* [Cu(acac)$_2$] as in Figure 5 (r 0.9985) showed $k_q\tau_o$ to be $1\,060 \pm 20$ l mol^{-1}. The two $k_q\tau_o$ values determined by different routes are in reasonably good agreement. This indicates that indeed singlet-excited benzene is sensitizing the photoreduction of the Cu(acac)$_2$ photoreduction. Using the reported lifetime of singlet excited-state benzene, $\tau_o = 29.5$ ns,[13] the quenching rate constant k_q is calculated to be 3.6—5.6 $\times 10^{10}$ l mol^{-1} s^{-1}. The interaction occurs therefore almost at a diffusion-controlled rate. It should be mentioned that ground-state complex formation between benzene and

$Cu(acac)_2$ was not detected in the concentration range 10^{-4}—3×10^{-3}M.

The results described above allow us to write a reaction scheme similar to that shown in equations (1)—(4). Equation (7) represents the interaction of singlet-state benzene and

$$^{*}C_6H_6 + Cu(acac)_2 \xrightarrow{k_q} [C_6H_6 - - - Cu(acac) - - - acac^{\bullet}] \quad (7)$$

$Cu(acac)_2$ which is proposed to occur by an energy-transfer mechanism since benzene has E_s 110 kcal mol^{-1}, a singlet-state energy sufficient to bring $Cu(acac)_2$ to its reactive excited state (254 nm excitation).[1,2] Equations (8) and (9) partition the

$$[C_6H_6 - - - Cu(acac) - - - acac^{\bullet}] + H_2 \longrightarrow C_6H_6 + Cu(acac) + acacH \quad (8)$$

$$[C_6H_6 - - - Cu(acac) - - - acac^{\bullet}] \longrightarrow C_6H_6 + Cu(acac)_2 \quad (9)$$

to a successful reduction and reversion to the ground state. This competition is what eventually determines the efficiency of the photoreduction. In view of the high bond energy of hydrogen (104 kcal mol^{-1}), a hydrogen-atom donation from hydrogen is surprising. It may occur through co-ordination with the copper centre which conceivably lowers the dissociation energy of the H_2 molecule.

Returning to benzophenone-sensitized photoreduction of $Cu(acac)_2$, it is established now that hydrogen can act as a hydrogen-atom donor [SH and R_2CO are H_2 and $(C_6H_5)_2CO$, respectively, in equation (2)] in the partition of the complex. An alternative mechanism to the $Cu(acac)_2$ photoreduction is to use the ketyl radical as a hydrogen-atom relay in this reduction [equations (10) and (11)]. This mechanism has been considered

$$^{*}[(C_6H_5)_2C{=}O] + S{-}H \longrightarrow (C_6H_5)_2\dot{C}{-}OH + S^{\bullet} \quad (10)$$

$$(C_6H_5)_2\dot{C}{-}OH + Cu(acac)_2 \longrightarrow (C_6H_5)_2C{=}O + Cu(acac) + acacH \quad (11)$$

to be unimportant on kinetic grounds[3] but has often been questioned. We can definitely eliminate this mechanism now on the basis of two observations. First, benzene does not abstract hydrogen from its excited states yet it sensitizes $Cu(acac)_2$ photoreduction just as efficiently as benzophenone. Secondly, benzophenone is not photoreduced when irradiated in benzene under hydrogen, indicating that the ketyl radical, as shown in equation (10), is not formed if H_2 is the hydrogen-atom donor SH. Therefore, the ketyl radical hydrogen-atom transfer, as shown in equation (11), is not involved in the photoreduction.

Acknowledgements

We acknowledge financial support provided by the Natural Sciences and Engineering Research Council of Canada.

References

1 G. E. Buono-Core, K. Iwai, Y. L. Chow, T. Koyanagi, A. Kaji, and J. Hayami, *Can. J. Chem.*, 1979, **57**, 8.

2 Y. L. Chow and G. E. Buono-Core, *Can. J. Chem.*, 1983, **61**, 795.

3 Y. L. Chow, G. E. Buono-Core, B. Marciniak, and C. Beddard, *Can. J. Chem.*, 1983, **61**, 801.

4 Y. L. Chow and G. E. Buono-Core, *J. Am. Chem. Soc.*, 1982, **104**, 3770.

5 H. D. Gafney and R. L. Lintvedt, *J. Am. Chem. Soc.*, 1971, **93**, 1623.

6 Y. L. Chow, G. E. Buono-Core, and Y. Shen, *Organometallics*, 1984, **3**, 702.

7 G. S. Hammond and P. A. Leermaker, *J. Phys. Chem.*, 1962, **66**, 1148.

8 (*a*) J. B. Birks, 'Photophysics of Aromatic Molecules,' Wiley-Interscience, London, 1970, pp. 84—139; (*b*) C. A. Parker, 'Photoluminescence of Solutions,' Elsevier, New York, 1968, p. 220.

9 For the details of the technique, see B. Marciniak, *J. Chem. Educ.*, submitted for publication.

10 I. B. Berlman, 'Handbook of Fluorescence Spectra of Aromatic Molecules,' Academic Press, New York, 1965, pp. 42—43.

11 P. B. Ayscough, 'Electron Spin Resonance in Chemistry,' Methuen, London, 1967, pp. 169—206.

12 H. Stephens and T. Stephens, 'Solubilities of Inorganic and Organic Compounds,' McMillan, New York, 1963, vol. 1.

13 J. B. Birks, In 'Organic Molecular Photophysics,' J. B. Birk, Wiley, London, 1975, vol. 2, pp. 409—597.

Received 13*th December* 1984; *Paper* 4/2114