PHOTOREACTIVITY OF LINEAR p-DIMETHYLAMINOBENZOYLATED POLYSTYRENE AND ITS MODEL COMPOUND, 4-DIMETHYLAMINO-4'-ISOPROPYLBENZOPHENONE

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Summary

Various aspects of the photochemical behaviour of linear p-dimethylaminobenzoylated polystyrene, 4-dimethylamino-4'-isopropylbenzophenone and of Michler's ketone have been studied in cyclohexane, benzene and chloroform. At low concentrations, the model compound is efficiently photoreduced in cyclohexane ($\phi = 0.58$), parallel to the behaviour of Michler's ketone ($\phi = 0.37$). Lower values were found in chloroform ($\phi = 0.12$) and in benzene ($\phi = 0.055$). The reduction quantum yield ϕ decreases as the model compound concentration increases and at concentrations higher than 10^{-4} M the quantum yield was found to be dependent on the extent of reaction, whereas it is independent in dilute solutions. A general kinetic scheme consistent with previous contributions to the subject and with our results has been proposed. In this scheme, a bimolecular hydrogen abstraction from the solvent with a second-order rate constant (k_r) competes with the triplet excimer formation (k_e) which is depopulated by two routes: physical deactivation to give the ground state ketones (k_{ed}) and hydrogen transfer (k_{er}) to give a pair of ketyl and aminomethyl radicals. The rate constants of hydrogen abstraction (k_r) in the three solvents studied were determined, as well as the ratio $k_{er}/(k_{er} + k_{ed})$ (approximately equal to 0.02) which measures the importance of hydrogen transfer through excimer formation. It is concluded that the excimer formation process leads principally to the generation of the starting ketone by physical deactivation, and only, to a small extent, to a pair of radicals via hydrogen transfer. Both ketones (the model compound and Michler's ketone) have similar lifetimes at room temperature and transfer their triplet excitation energy to naphthalene and *trans*-stilbene with high rates. In contrast with this behaviour, the polymeric sensitizer shows very low reactivity and its energy donor ability is quite limited. These results can be explained by the efficient intramolecular self-quenching which takes place in the functionalized macromolecules owing to the large local concentration of chromophore.

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1. Introduction

The potential use of polymer-bound photosensitizers in photochemical reactions has promoted the study and development of these promising functionalized polymers.

Michler's ketone (MK) and 4-(N,N'-dimethylamino)benzophenone, as well as other similar compounds, constitute a known and important family of photosensitizers. They present an intense absorption with a maximum between 300 and 400 nm (molar extinction coefficient greater than 20 000 $cm^{-1} \, mol^{-1}$) which permits the use of very low sensitizer concentrations [1, 2].

Hautala and Little [1] have functionalized two solid and insoluble matrices with dimethylaminobenzophenone and the resulting immobilized photosensitizers have been tested for their potential use in the norbornadiene–quadricyclene solar energy storage reaction.

Linear polystyrene, conveniently functionalized, is being currently used in our laboratory as a support for different sorts of molecular species which are recognized as efficient photosensitizers [3]. The linear character of such polymeric supports allows evaluation of their sensitizing properties to be effected in homogeneous solutions, a condition which facilitates the achievement of quantitative measurements, particularly those concerning light absorption.

In a recent paper [4] we have reported the preparation of linear p-dimethylaminobenzoylated polystyrene (PS–MI) and its model compound, 4-isopropyl-4'-N,N-dimethylaminobenzophenone (CU–MI) (see structures below).
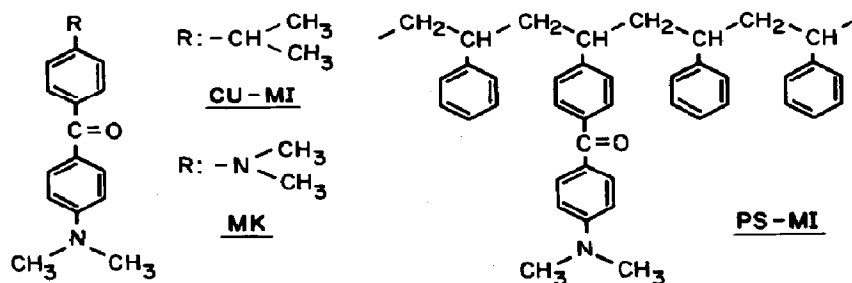
We report here on the photochemical behaviour of the two compounds with regard to photoreduction and energy transfer processes.

2. Experimental details

2.1. Materials

Linear PS–MI and its model compound CU–MI were prepared according to the method described in ref. 4. The functionalized polymer

used in the present work had a chromophore content of 10% and a weight-average molecular weight of 200 000. MK was supplied by Aldrich and its purification procedure involved three stages of solubilization in dilute HCl, filtration and precipitation with NH_3. Finally the samples were recrystallized three times from hot ethanol—water. The solvents used for the irradiations (cyclohexane, benzene, chloroform and dimethylformamide (DMF)) were spectroscopic grade from Merck. Benzene and chloroform (fluorescence grade) from Carlo Erba were used for the luminescence measurements without further purification. The cyclohexane (fluorescence grade, from Carlo Erba) used for luminescence measurements was washed in turn with concentrated sulphuric acid, sodium carbonate solution and distilled water. It was dried over anhydrous magnesium sulphate and then over sodium and finally it was distilled prior to use. Naphthalene, used as a quencher, was purified by sublimation. Stilbene (trans and cis), provided by Aldrich as a high purity product, was used without further purification.

2.2. Irradiation procedure

The irradiation device consisted of an optical bench, including a xenon lamp (Osram XBO 900 W), monochromator, quartz lens, light filters and a cell holder maintained at a constant temperature of 30 °C. A radiometer placed immediately behind the cell allowed changes in the light intensity to be measured. An Aberchrome 540 (Edward Davids Chemical Laboratories) actinometer was used to relate the digital display of the radiometer to an absolute value for the number of quanta incident per unit time [5]. The samples contained in a Pyrex glass tube joined to a quartz cuvette were degassed with three freeze—degas—thaw cycles. The volumes of solution in the irradiation experiments were 4 ml in the cell with path length 10 mm and 0.4 ml in the cell with path length 1 mm. The kinetics of the charge transfer band disappearance were obtained by taking readings of absorbance at the maximum of the charge transfer band (330 - 350 nm, depending on the sample and the solvent) at different times of irradiation (λ_i of 360 and/or 380 nm). After the spectrophotometric readings, the samples were again placed in the holder and left to reach the equilibrium temperature before restarting irradiation. The trans—cis stilbene isomerization was monitored by taking readings of the absorbance at 287 nm (benzene) and at 304 nm (chloroform). These wavelengths corresponded to the isosbestic points observed in the reduction process. Spectra and absorbance measurements were recorded using a Perkin—Elmer 554 spectrophotometer.

A high performance liquid chromatography (HPLC) apparatus (model M-45 Waters high pressure pump, with a U6K injector and a Philips—Pye—Unicam PU4020UV detector) was used to measure the cis-stilbene in the work carried out at a trans-stilbene concentration of 10^{-3} M. Details of the method have been published elsewhere [5].

2.3. Phosphorescence lifetimes

Phosphorescence measurements were conducted at room temperature employing thoroughly degassed samples dissolved in benzene, cyclohexane and chloroform. Emission was monitored 90° to the excitation axis through the monochromator set at the wavelength for maximum phosphorescence intensity using a Perkin–Elmer LS-5 luminescence spectrometer connected to a Model 3600 data station. The phosphorescence intensity was monitored at delay times of 40, 50, 60, 70, 80 and 90 μs (excitation wavelength, 340 nm).

2.4. Pinacol determination

Some irradiated samples were analysed for pinacol in order to assure that this compound was the main product of the photoreaction. Reoxidation by treatment with alkali according to a published procedure [6] allowed us to confirm this point. Pinacol accounts for more than 90% of the ketone disappearance in the case of dilute solutions of CU–MI.

3. Results

3.1. Quantum yields of CU–MI disappearance

As in the case of MK [7], irradiation of CU–MI in cyclohexane gives rise to a decrease in the charge transfer band at 331 nm and thus to an increase in absorption at 270 nm. An isosbestic point is observed at 295 nm (Fig. 1). The quantum yield of the CU–MI disappearance, measured by the decrease in absorbance of its charge transfer band, is as high as 0.58 when the concentration is below 5×10^{-5} M and pure well-degassed samples are used. When irradiations are carried out at concentrations higher than 10^{-4} M, an increase in absorbance in the region 390 - 412 nm is observed, together with the appearance of a new isosbestic point at 385 nm.

Under the last conditions, the quantum yield was found to be dependent on the extent of reaction, whereas in dilute solutions it remained constant up to conversions of about 56% - 60%. Values of 0.20 and 0.17 were obtained employing initial concentrations of 5×10^{-4} M and 5×10^{-3} M respectively, and conversions lower than 10%.

The quantum yield of MK was also determined for comparison purposes. Employing a thoroughly purified sample (10^{-5} M), a value of 0.37 resulted, which agrees well with those reported by Suppan [7] (0.38) and Schuster et al. [8] (0.40). As before, a higher MK concentration leads to a lower quantum yield.

Similar results are achieved when chloroform is substituted for cyclohexane (Fig. 1, Table 1), although the quantum yield undergoes a pronounced diminution. An even larger decrease occurs in benzene solution but, unlike in the foregoing cases, no absorption at longer wavelengths developed during irradiation and the quantum yields can be measured at relatively high conversions. This fact allowed reliable determinations of
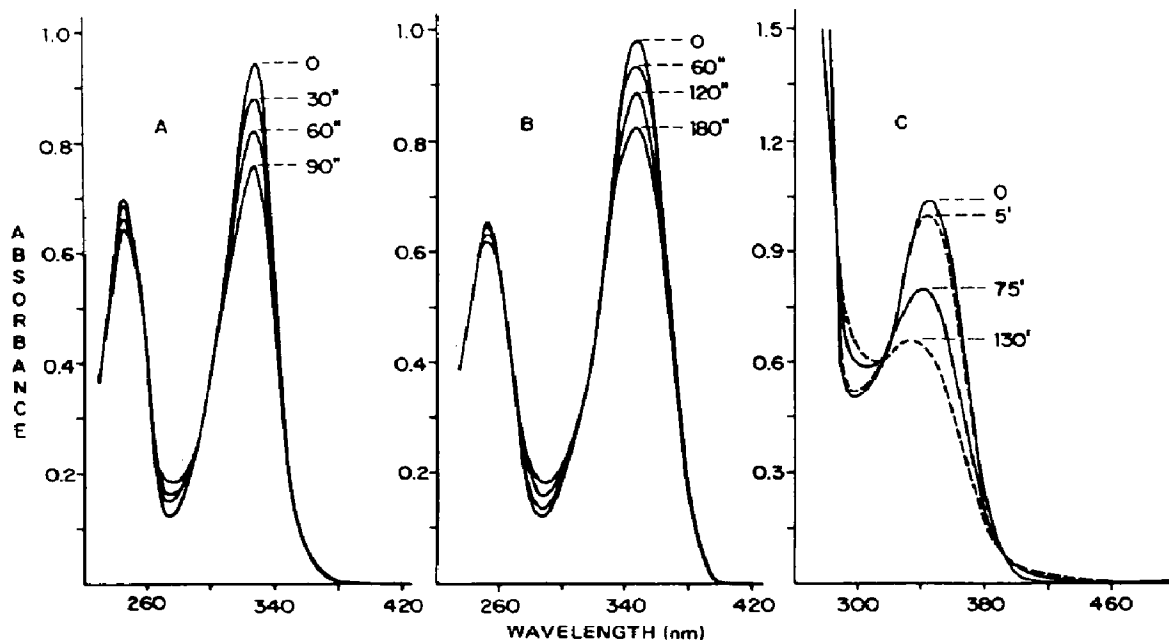
Fig. 1. Absorption spectra of CU–MI and PS–MI at various stages of irradiation: (a) a solution of CU–MI in cyclohexane (molar concentration, 4×10^{-5}; irradiation wavelength, 360 nm; incident light flux, 2.9×10^{-9} einsteins s^{-1}); (b) a solution of CU–MI in chloroform (molar concentration, 4.3×10^{-5}; irradiation wavelength, 380 nm; incident light flux, 4×10^{-9} einsteins s^{-1}); (c) a solution of PS–MI in chloroform (chromophore molar concentration, 4.6×10^{-5}; irradiation wavelength, 380 nm; incident light flux, 2.9×10^{-9} einsteins s^{-1}).

the quantum yield in concentrated solutions. Finally, the use of DMF showed that CU–MI is practically unreactive in this polar solvent.

Quantum yield determinations for the polymeric sensitizer PS–MI presented more difficulties. The appearance of the long-wavelength band at around 400 nm takes place even in dilute solutions and the quantum yield becomes very sensitive to the extent of reaction, probably owing to the inner-filter effect of the absorbing byproducts formed. Nevertheless, initial values obtained at conversions less than 5% clearly bring out their strong diminution with respect to the monomeric sensitizers (Fig. 1, Table 1).

3.2. Electronic energy transfer to naphthalene and trans-stilbene

The characterization of CU–MI and PS–MI as energy donors has been carried out with the aid of naphthalene and trans-stilbene. These energy acceptors possess triplet energies ($E_T = 61$ kcal mol^{-1} and $E_T = 50$ kcal mol^{-1} respectively) which are similar to, and lower than, those corresponding to the donors if it is assumed that the donors and MK ($E_T = 61$ kcal mol^{-1}) have equivalent excited triplet energy levels.

Energy transfer to naphthalene has been studied by monitoring the ratio ϕ_0/ϕ_q, i.e. the ratio of the quantum yields of the disappearance of the

TABLE 1

Lifetimes and quantum yields of disappearance for CU–MI, MK and PS–MI

Solvent	$[S_0] \times 10^5$ (M)	$\tau \times 10^6$ (s)	ϕ_{ex}	ϕ_{cal}
CU–MI				
Cyclohexane	4.0	33	0.58	0.58
Cyclohexane	50.0		0.20	0.25
Cyclohexane	100.0		0.17	0.16
Chloroform	4.8	30	0.12	0.12
Benzene	1.1	37	0.055	0.056
Benzene	5.0		0.050	0.050
Benzene	10.0		0.040	0.045
Benzene	100.0		0.025	0.026
DMF	5.5		less than 10^{-3}	
MK				
Cyclohexane	1.1	32	0.37	0.36
Cyclohexane	50.0		0.15	0.16
Chloroform	1.1	28	0.07	0.07
PS–MI				
Chloroform	4.5	10	0.010	0.01
Benzene	1.1	10	0.008	0.02
DMF	1.1		10^{-3}	

sensitizer in the absence and presence of the quencher. Typical Stern–Volmer plots are shown in Fig. 2. As can be seen, MK and CU–MI transfer energy in chloroform equally efficiently, in accordance with the assumption made above. However, the Stern–Volmer constant k_{SV} obtained for MK in cyclohexane (see Table 2) is close to 1.8×10^5, Suppan's reported value [7].

The aforementioned difficulties found in the determinations of the quantum yield for the polymeric sample precluded an accurate evaluation of its k_{SV} value. In fact, the attempted Stern–Volmer representation (not shown in Fig. 2) was not linear. We have included in Table 2 only a rough estimate of the k_{SV} value. Whichever is the correct value, it is apparent that a dramatic decrease in energy transfer efficiency occurs in going from the monomeric to the polymeric sensitizer.

An analogous result is achieved when *trans*-stilbene is used instead of naphthalene. In this case, the rate of *trans*-stilbene isomerization is given by the following simplified expression:

$$- \frac{d[trans\text{-stilbene}]}{dt} = \phi_{ST} I_a \frac{k_{SV}[trans\text{-stilbene}]}{1 + k_{SV}[trans\text{-stilbene}]} \phi_{tc} = \phi_{ST} I_a \gamma_{ET} \phi_{tc} \qquad (1)$$

where I_a (einsteins s^{-1} l^{-1}) is the intensity of light absorbed, γ_{ET} is the efficiency of the energy transfer step, and ϕ_{ST} and ϕ_{tc} are the quantum yields of intersystem crossing and of triplet *trans*–cis isomerization (0.55) [5] respectively. This formula is only valid for the first stages of the process, *i.e.* when
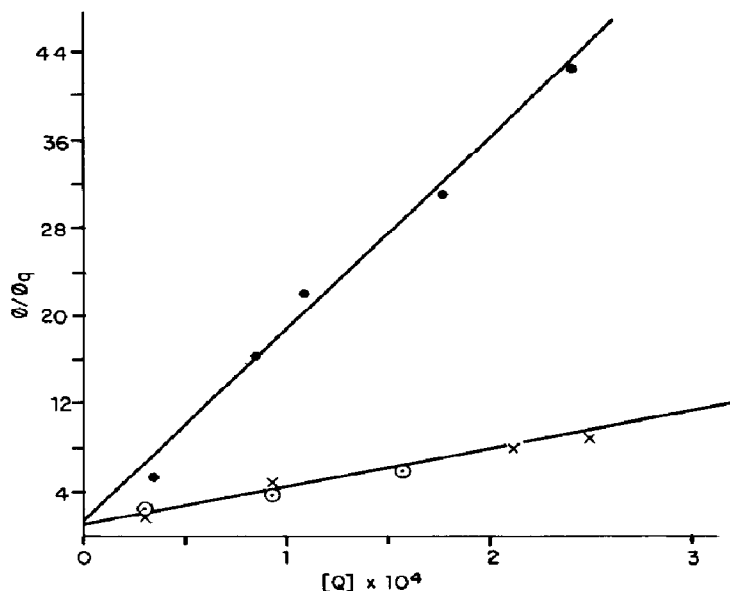
Fig. 2. Kinetic data for the quenching of the photoreactivity of CU–MI and MK by naphthalene: ●, MK–naphthalene in cyclohexane; ⊙, MK–naphthalene in chloroform; ×, CU–MI–naphthalene in chloroform.

TABLE 2

Energy transfer parameters

Photosensitizer	Solvent	[Naphthalene] $\times 10^5$ (M)	k_{SV} (M^{-1})
MK	Cyclohexane	2.4 - 24.0	172000
MK	Chloroform	3.1 - 25.0	30000
CU–MI	Chloroform	3.1 - 25.0	30000
PS–MI	Chloroform	50 - 1000	600

the reversibility can be ignored. Under this condition, γ_{ET} remains approximately constant and a plot of the *trans*-stilbene concentration *vs.* the absorbed energy E_a (equal to $I_a t$) should give a straight line. These plots are shown in Fig. 3, and Table 3 collects the values of the slopes which are related to the product $\phi_{ST}\gamma_{ET}$.

Those kinetic runs effected by using dilute solutions of the quencher were monitored by absorption spectrophotometry of *trans*-stilbene. The determinations carried out at a high quencher concentration were performed by HPLC analysis of *cis*-stilbene. These latter experiments were designed to determine ϕ_{ST}, since work under exceedingly high quencher concentrations would assure γ_{ET} values equal to unity. An inspection of the values obtained shows the high efficiency with which the energy is transferred to

TABLE 3

Energy transfer parameters

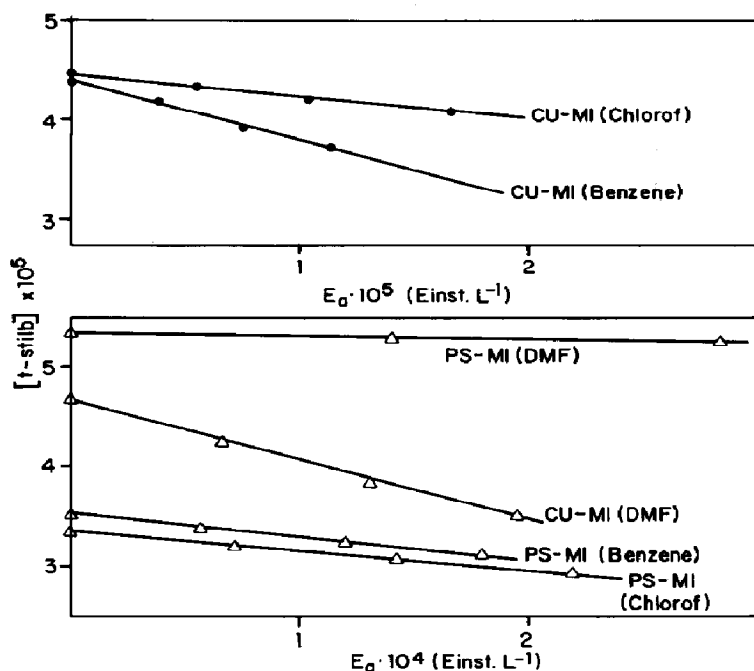| Photosensitizer	Solvent	[trans-Stilbene] × 10^5 (M)	$\phi_{ST} \times \gamma_{ET}$
CU–MI	Benzene	3.5	1.06
CU–MI	Benzene	230.0	0.99
CU–MI	Chloroform	4.5	0.41
CU–MI	Benzene	230.0	0.47
CU–MI	DMF	4.7	0.11
PS–MI	Benzene	3.5	0.032
PS–MI	Chloroform	3.4	0.030
PS–MI	DMF	4.4	0.0047

Fig. 3. Plots of the trans–cis isomerization of stilbene for the first stages of the process *vs.* absorbed energy.

the quencher, *trans*-stilbene, in the case of the monomeric sensitizers while, as before, the polymeric sample affords very poor results. It is worth noting that ϕ_{ST} for CU–MI in chloroform amounts to only 0.47, well below the value of unity found in benzene. MK in benzene and in cyclohexane also affords the high values of 1.0 and 0.91 respectively for the intersystem crossing quantum yields [8].
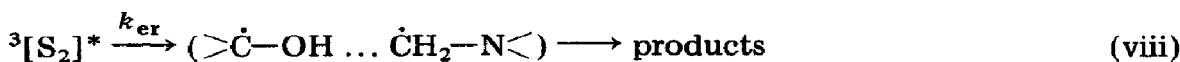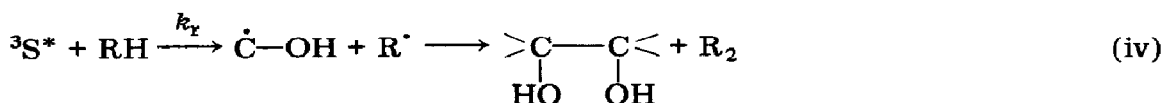
3.3. Lifetimes

The triplet lifetimes for CU–MI in benzene and in chloroform and for MK in cyclohexane are included in Table 1. They were obtained by monitoring the phosphorescence decay of extremely well degassed solutions. The lifetime corresponding to the polymeric sample is expected to be short enough to be beyond the detection limit of the apparatus and therefore could not be determined.

4. Discussion

A general kinetic scheme [7] consistent with previous contributions to the subject [7 - 14] and with our own results is as follows:

$$S_0 \xrightarrow{I_a} {}^1S^* \tag{i}$$

$$^1S^* \xrightarrow{I_a\phi_{ST}} {}^3S^* \tag{ii}$$

$$^3S^* \xrightarrow{k_d} S_0 \tag{iii}$$

$$^3S^* + RH \xrightarrow{k_r} \dot{C}-OH + R^{\cdot} \longrightarrow \underset{HO}{>}C-\underset{OH}{C}< + R_2 \tag{iv}$$

$$^3S^* + Q \xrightarrow{k_q} S_0 + Q^* \tag{v}$$

$$^3S^* + S_0 \xrightarrow{k_e} {}^3[S_2]^* \tag{vi}$$

$$^3[S_2]^* \xrightarrow{k_{ed}} 2S_0 \tag{vii}$$

$$^3[S_2]^* \xrightarrow{k_{er}} (>\dot{C}-OH \ldots \dot{C}H_2-N<) \longrightarrow products \tag{viii}$$

where S_0 stands for the ground state ketone and RH for the solvent.

In this scheme, processes (i) - (v) correspond to the usual behaviour of aromatic carbonyl compounds in solution. The excited triplet state is depopulated by unimolecular physical decay, kinetically governed by the intrinsic rate constant k_d, and by a bimolecular hydrogen abstraction from the solvent with a second-order rate constant k_r. In the case of benzophenones, this reaction leads to benzopinacols as final products via combination of the primary ketyl radicals. Energy transfer to a quencher Q, occasionally present in the solution, is another common way of triplet depopulation.

It has been proposed that the formation of a triplet excimer [7, 8], or exciplex [15], between the excited and ground states of the MK would account for its very efficient self-quenching. Although the existence of such an excited triplet complex has not been proved, there are numerous studies

on the photochemistry of aromatic ketones and amines [16 - 22] which render strong support to the proposal. Route (vi) in the scheme illustrates this possibility. Processes (vii) and (viii) provide two possible decay mechanisms for the complex. Process (vii) would give directly the ground state ketones and therefore represents an apparently simple physical quenching of the excited triplet state. Process (viii) leads to a pair of ketyl and aminomethyl radicals. Predictions about the subsequent fate of the two radicals involves a great deal of uncertainty. If they diffuse apart, a logical outcome could be the ketyl combination to give benzopinacol, on the one hand, and the aminomethyl hydrogen abstraction from the solvent to generate the starting ketone, on the other hand. Hence, the net chemical result would be a photoreduction of the ketone mediated by itself. Different sorts of products can be obtained if the radicals have the necessary time to react before leaving the solvent cage. Disproportionation, for example, would provide another pathway to generate the starting compounds. Radical combination could give a "normal" coupling dimer I or an unstable species II, known in the literature as a light-absorbing transient (LAT), which is ascribed to a para- or an ortho- radical coupling, although the exact nature of its structure has not yet been elucidated [23].
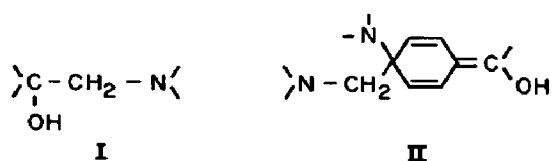
The formation of LATs interferes with the spectroscopic evaluation of ketone consumption since LATs absorb in the analytical region. Inner-filter effects result from the appearance of LATs during irradiation, making the quantum yield determinations more difficult.

The overall observed quantum yield of ketone disappearance, ϕ_{ex}, is given by eqn. (2):

$$\phi_{ex} = \phi_{ST} \frac{k_r^* + \alpha k_e[S_0]}{k_r^* + k_d + k_e[S_0]} \tag{2}$$

In this expression, k_r^* is the pseudo-first-order rate constant for triplet decay by direct hydrogen abstraction from the solvent, and $\alpha k_{er}/(k_{er} + k_{ed})$ measures the importance of reduction through complex formation. The triplet character of the reaction and its reductive nature have been corroborated by the quenching experiments and by the analysis of benzopinacols in the irradiated solutions and our results will be rationalized within the framework of these ideas.

Our attention will be first focused on the values obtained for the quantum yield of CU–MI or MK, the quantum yield of disappearance, ϕ_{ex}, and the triplet lifetimes τ which are shown in Table 1. It is apparent that the ϕ_{ex} undergo a diminution when the ketone concentration is increased.

Nevertheless, as indicated in Section 3, the quantum yield does not vary with the extent of conversion if the initial benzophenone concentration is maintained at 5×10^{-5} M. This result means that the contribution to the overall kinetics from processes (vi) - (viii) is small if irradiation is conducted employing such dilute solutions. Therefore, eqn. (2) can be approximated by

$$\phi_{ex} = \phi_{ST} \frac{k_r^*}{k_r^* + k_d + k_e[S_0]_0} = \phi_{ST}k_r^*\tau \tag{3}$$

where $[S_0]_0$ is the lowest ketone concentration utilized. The self-quenching term in the denominator has been maintained because it was experimentally obtained at that concentration. The determination of an extrapolated τ value at zero concentration was not feasible.

The CU—MI intersystem crossing efficiency ϕ_{ST} drops from 1.0 in benzene to 0.47 in chloroform. This decrease is clearly appreciated in the quenching experiments carried out with stilbene (Table 3). The observed decrease is accentuated if we take into account the halogenated character of the latter solvent which would, in principle, favour intersystem crossing. Actually, this result cannot be considered as entirely unexpected, because solvent effects on the photochemistry of p-amino-substituted benzophenones are known from the earliest reports by Porter and Suppan [9, 10] and continue to be a matter of active discussion. However, the accent has always been put on the relationship between the reactivity of the lowest triplet (normally against a hydrogen donor) and its electronic configuration. Schuster *et al.* [8] pointed out the importance of the intersystem crossing process after noting the decrease in ϕ_{ST} for MK on going from an aprotic solvent (benzene, cyclohexane) to a protic solvent (2-propanol, ethanol). Our finding represents another example of the influence of solvent and suggests that other effects besides those derived from hydrogen bonding must be considered to explain the differences observed.

In order to calculate the rate constant k_r^* corresponding to both CU—MI and MK, we assumed that the two compounds possess the same ϕ_{ST}, *i.e.* 0.91 in cyclohexane (the reported value for MK [8]) and 0.47 in chloroform (the value obtained for CU—MI in the present work). The estimated k_r^* values are collected in Table 4 together with other parameters of interest. Division of the k_r^* values by the solvent molarities affords the bimolecular reactivity constants, k_r, which are the parameters commonly submitted for comparison. Estimates of $k_e[S_0]_0$ values (see below) have also been included.

An inspection of all the values in Table 4 confirms the expected reduced reactivity of the lowest triplet of CU—MI compared with that of the unsubstituted benzophenone. For instance, the unsubstituted benzophenone reacts in cyclohexane with $k_r = 7.2 \times 10^5$ M^{-1} s^{-1} [24]. The reactivity decrease is slightly less pronounced than in the case of MK, most likely reflecting the electron donating ability of the second dimethylamino group which exists in MK.

It is worthwhile to note that substitution of chloroform for cyclohexane reduces the k_r value by a factor of about 3 for both CU—MI and MK.

TABLE 4

Calculated kinetic parameters for MK and CU–MI triplets

Solvent	$[S_0]_0 \times 10^5$ (M)	$1/\tau \times 10^{-4}$ (s^{-1})	$k_r^* \times 10^{-4}$ (s^{-1})	$k_e[S_0]_0 \times 10^{-4}$ (s^{-1})	$k_r \times 10^{-3}$ ($M^{-1} s^{-1}$)
CU–MI					
Cyclohexane	4.0	3.03	1.93	0.36	2.08
Chloroform	4.8	3.33	0.85	0.77	0.68
Benzene	1.1	2.70	0.15	0.14	0.13
MK					
Cyclohexane	1.1	3.13	1.27	0.10	1.37
Chloroform	1.1	3.57	0.53	0.18	0.42

The slight polarity of chloroform might contribute to this diminution of reactivity by making more important the $\pi\pi^*$ or charge transfer character of the lowest triplet, an influence generally admitted but whose details are not yet completely understood [7, 8, 14]. However, the ability of the solvent to donate hydrogen is another factor which must be taken into account. In this case, cyclohexane and chloroform ought to have similar hydrogen-donor character judging from their C—H bond energies, about 95 kcal mol^{-1} [25]. Actually, if we follow the normal practice in studying hydrogen abstraction reactions by comparing experimental overall rate constants in terms of rate constants per hydrogen atom [24], our results would indicate that chloroform is indeed a better hydrogen donor.

The order found for the CU—MI reactivity in cyclohexane and that in benzene agrees well with the known poor hydrogen-donating ability of benzene. However, the observed k_r value in benzene is only slightly smaller than that reported for benzophenone, 0.16×10^3 M^{-1} s^{-1} [26]. This fact probably stems from the different mechanism by which benzene gives up its hydrogen to a triplet ketone [27, 28]. We lack complete information for DMF but the data included in Table 1 indicate that in this solvent the triplets are practically unreactive.

The decrease in ϕ_{ex} as a function of the ketone concentration (see Table 1) might be quantitatively justified if the rate constants for complex formation, k_e, could be evaluated. As a trial, we have considered the reported value for MK in benzene (1.3×10^8 M^{-1} s^{-1} [8]) to be valid also for CU—MI in the same solvent. The ratio between this value and that corresponding to the limiting diffusion case (10^{10} [29]) has been used as a criterion to forecast the k_e values concerning cyclohexane and chloroform, i.e. 0.9×10^8 M^{-1} s^{-1} and 1.6×10^8 M^{-1} s^{-1} respectively. Equation (4) can now be used to estimate the quantum yield of ketone disappearance, ϕ_{cal}, for any concentration $[S_0]$:

$$\phi_{cal} = \phi_{ST} \frac{k_r^* + \alpha k_e[S_0]}{\tau^{-1} + k_e([S_0] - [S_0]_0)} \qquad (4)$$

where $[S_0]_0$ stands for the lowest concentration employed and k_r^* and r are the experimental parameters obtained making use of eqn. (3). Since a good fit of the experimental and calculated values of ϕ is achieved (see Table 1) when $\alpha \approx 0.02$, we can safely conclude that the complex-formation process (vi) leads principally to a generation of the starting ketone by physical quenching of the triplets, process (vii), and only to a small extent to a reductive disappearance of the latter via route (viii). In connection with this point, it is worthwhile to remark that the calculation of k_r^* by means of the approximated eqn. (2) turns out to be completely justified only because of the low value of α. Indeed, if our guesses for the k_e values are not far from the true values, the exclusion of the term $k_e[S_0]_0$ in the numerator of eqn. (2) to go to eqn. (3) should not be permitted for large values of α. We can see in Table 3 that pathways (iv) and (vi) may become competitive even when employing such dilute solutions.

A final comment on the results corresponding to the models concerns the rate constants of the quenching by naphthalene. These constants, k_{ET}, are simply obtained from the Stern–Volmer constants (see Table 1) using the relation $k_{ET} = k_{SV}/\tau$. The afforded values, 5.3×10^9, 1.1×10^9 and 1.0×10^9 M^{-1} s^{-1} respectively for MK in cyclohexane and in chloroform and for CU–MI in chloroform indicate that energy transfer is more rapid in the first solvent where the process is virtually diffusion controlled. This fact suggests that chloroform could decrease the exothermicity of the energy transfer step by making the triplet donor less energetic.

We can now proceed to examine the results which correspond to the polymeric photosensitizer. On the whole, this sensitizer is characterized, on the one hand, by a poor ability to transfer energy and a lack of reactivity *vs.* hydrogen abstraction and, on the other hand, by its tendency of LAT formation.

The first properties can be easily explained if we apply the local concentration concept. The concentrations of the polymeric solutions appearing in Tables 2 and 3 are referred to as the overall chromophore concentrations. But if we bear in mind the chromophore content (10%) of the macromolecules and their weight-average molecular weight, 2×10^5, with an average radius of gyration of 134 Å, a straightforward calculation affords a figure of 3×10^{-2} M for the chromophore concentration within the volume encompassed by a macromolecule. The high value of this local concentration makes intramolecular self-quenching the predominant pathway and explains why neither hydrogen abstraction nor energy transfer are relevant processes. In fact, eqn. (4) affords a limiting value for ϕ_{cal} equal to $\phi_{ST}\alpha$ if we introduce in it the large value corresponding to the local concentration. The values included in Table 1, 0.01 in chloroform and 0.008 in cyclohexane, are in accordance with such expectations.

The other feature which needs to be interpreted in the case of the polymeric samples is the tendency of LAT formation. Apparently, the importance of route (vi) in the triplet deactivation would facilitate LAT formation through route (viii). Hence, it is tempting to ascribe this tendency to a

simple concentration effect. To ascertain the validity of such a simple explanation, several irradiations of very concentrated solutions of the models were carried out. Although the formation of light-absorbing products increased with concentration, the amount produced was much less important than in the case of the polymeric sensitizer, a fact clearly evident from the different intensities of the colour (light yellow) displayed in the irradiated solutions. Therefore, an intrinsic effect due to the polymeric nature of the sensitizer must play a role in the increased tendency to form an LAT.

In a recent investigation, Scaiano *et al.* [30] have studied the photoreduction of benzophenone in sodium dodecylsulphate and other surfactant micelles and the results were compared with those obtained in homogeneous cyclohexane solutions. They observed a substantially enhanced LAT formation in the micellar case. Two basic ideas were set forth to account for the enhanced effect. Firstly, the interaction time between the two radicals formed after the primary hydrogen abstraction step increased. The radical pair finds a barrier over which to escape from the micelle and, consequently, has more opportunities to react either by coupling or by disproportionation. Secondly, the micro-environment exerts control over the final partition of the radical pair into products.

It appears to us that this kind of reasoning might apply, at least in a qualitative way, to the polymer case. We consider the formation of the triplet complex as taking place between the triplet excited ketone and another ground state ketone pendant to the same macromolecule. The relative importance of processes (vi) - (viii) and, above all, the nature of the products arising from the last process could obviously be influenced by their intramolecular character. Our results indicate that route (vii) continues to be the preferential mode of complex dissociation and pathway (viii) leads to predominantly para or ortho coupling.

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