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PHOTOINITIATION MECHANISM OF ACRYLAMIDE POLYMERIZATION IN THE PRESENCE OF WATER-SOLUBLE BENZOPHENONES

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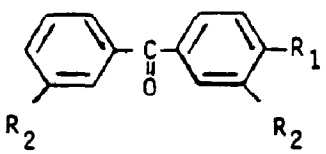
Summary

Water-soluble benzophenones were used to induce the photopolymerization of acrylamide in homogeneous solution. The determination of the processes in the excited states (through laser spectroscopy) forms a basis for the discussion of the photoinitiation step of the reaction as well as the specific interactions of cationic and anionic derivatives with the monomer. It was found that sulphonated benzophenones can initiate the photopolymerization of acrylamide efficiently without any additives.

1. Introduction

During recent years there has been considerable interest in the field of water-soluble photoinitiators [1, 2]. The derivatives of benzophenone containing trimethylammonium chloride and sodium sulphate groups (BP^+, BP^-, BP^{2-}) are especially suitable for photoinitiating the polymerization of acrylamide (AA) in water solutions or in reverse micellar assemblies.

The photochemistry of benzophenone and its behaviour as an initiator of photopolymerization of many acrylic and methacrylic monomers in homogeneous [3 - 5] and microheterogeneous media [6, 7] is well known.



	R_1	R_2
BP^+	$-CH_2N(CH_3)_3Cl$	$-H$
BP^-	$-CH_2SO_3Na$	$-H$
BP^{2-}	$-H$	$-SO_3Na$

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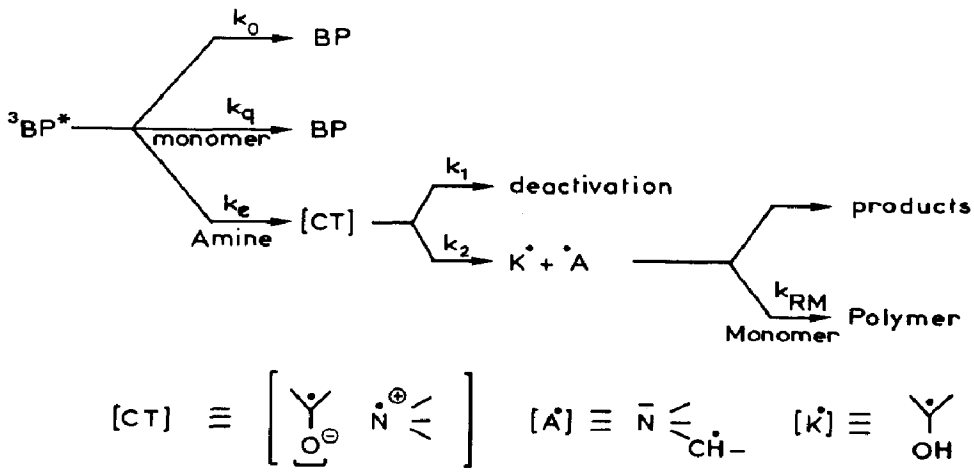
Photoexcitation of BP leads to the triplet state (^{3}BP) which decays according to the reactions shown in Scheme 1. k_0 is the first-order rate constant of the spontaneous decay, k_q is the constant for quenching by monomer (leading via CT_2 either to the species in their fundamental singlet states through an energy transfer process or to the initiation of polymerization with low efficiency [8]) and k_e is the bimolecular rate constant for quenching by amine A (corresponding to the formation of a charge transfer complex CT_1 by electron transfer from the amine lone pair to the carbonyl group of the ketone which mainly deactivates through a proton transfer process which generates free radicals). With the objective of checking whether the photoinitiation by BP^+, BP^- and BP^{2-} occurs according to the same mechanism and to compare the efficiencies of the initiators, we undertook the present investigation of the photopolymerization of AA in aqueous solutions containing amines and the photoinitiators, and also studied the excited states involved.



Scheme 1.

2. Experimental details

The water-soluble benzophenones BP^+ and BP^- prepared as described in ref. 9 were obtained as a gift from Ward Blenkinsop. BP^{2-} was prepared by the following procedure. 20 g benzophenone was dissolved in 200 g fuming sulphuric acid containing 20% SO_3 and was heated up to 150 °C for 4 h. Then the reaction mixture was poured into 400 g ice and neutralized by addition of $CaCO_3$. After filtration, the solution was evaporated under reduced pressure until an oily liquid remained. Upon addition of 30 g $BaCl_2 \cdot 2H_2O$ the crude barium salt of BP^{2-} was isolated, and it was then recrystallized three times from water. The desired sodium salt, which is highly water soluble, was obtained by addition of a calculated amount of sodium carbonate to an aqueous solution of the barium salt. After filtration

of the $BaCO_3$ precipitate, the filtrate was evaporated to dryness. AA (Janssen Chimica), trimethylamine (TEA) and triethanolamine (TEOH) (Aldrich) were used as received.

The water solutions of AA containing the photoinitiators were degassed by bubbling nitrogen through them. The concentrations of BP^- and BP^+ were adjusted so that the optical densities were 0.2 at 366 nm (steady state experiments) and 0.5 at 347 nm (laser spectroscopy). Continuous photolysis was performed as described previously [5] with a high pressure mercury lamp which gave an incident light intensity in the range $(0.8 - 7) \times 10^{-6}$ einsteins l^{-1} s^{-1}. After illumination, polyacrylamide was precipitated from the water on adding acidified methanol. The conversion was determined gravimetrically and the polymerization rate R_p was deduced from the linear part of the time–conversion curve.

The technique of mode-locked ruby laser spectroscopy used in this work has been described previously [10]. The triplet state lifetime $^3\tau$ and the constants for quenching by AA and TEA were determined from the classical Stern–Volmer plot.

The aqueous solutions of AA containing BP^{2-} were degassed by bubbling nitrogen through them. The concentration of BP^{2-} was 10^{-2} M in the polymerization experiments and 10^{-3} M in the flash photolysis studies. Experiments under continuous illumination were performed with a merry-go-round apparatus which included a medium pressure mercury lamp and a filter combination which was only transparent to the 365 nm line. The incident light intensity I_0 was 1.6×10^{-5} einsteins l^{-1} s^{-1}. After illumination, the conversion of monomer was determined by titration of the unreacted double bonds. Polymerization rates and quantum yields were calculated from the linear part of the time–conversion curve.

The triplet lifetime of BP^{2-} was determined by using a xenon flash spectrometer as described in ref. 11. The absorption of the triplet state was always accompanied by a certain amount of ketyl radical absorption and since no complete spectral separation was possible the lifetime of the ketyl radical had to be considered in the calculation of $^3\tau$. The constant for quenching by AA was obtained by monitoring the decay of the initial ketyl radical absorption upon addition of AA.

3. Results and discussion

3.1. Steady state illumination

3.1.1. Per cent conversion vs. time

As can be seen in Fig. 1, a linear time dependence is observed for the acrylamide conversion up to about 40%. The rate R_p of polymerization with ketone–amine systems is high (typically $(100 - 600) \times 10^{-5}$ M s^{-1}). The quantum yield ϕ_m of the polymerization, which is defined as the number of starting chains per absorbed photon and which corresponds to the ratio between R_p and the incident light intensity absorbed, lies in the range

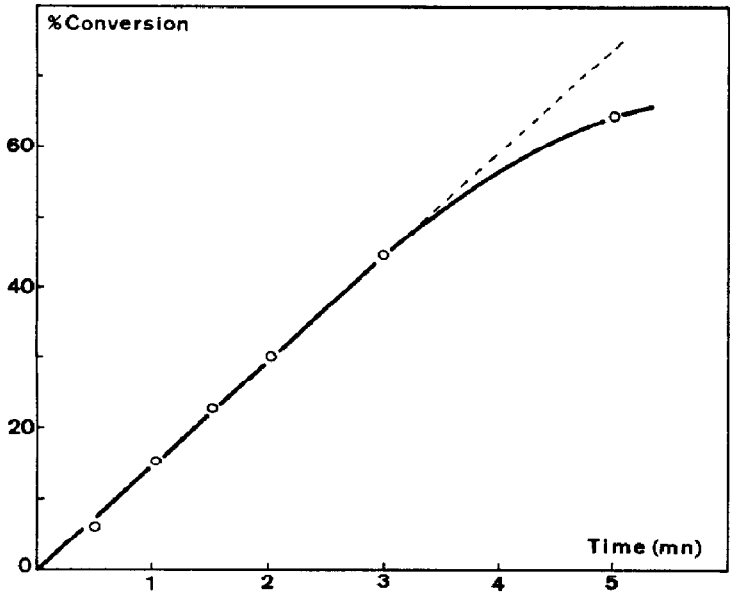


Fig. 1. Time dependence of percentage conversion of AA in aqueous solution (initiator, BP^+; [AA] = 0.7 M; $I_0 = 4 \times 10^{-6}$ einsteins l^{-1} s^{-1}; [TEA] = 0.05 M).

300 - 2000; such high values are mainly due to the high value of $k_p/k_t^{0.5}$ for AA (about 4.7 $M^{-1/2}$ $s^{-1/2}$ [12]).

It is also observed that the photoinitiation can take place in the absence of amine: in the case of BP^-, polymerization develops with a rate about three times lower than in the system BP^-–TEA. With BP^+, the difference is so great that only traces of polymer are formed in the absence of amine (the relative rates being in the ratio 1:10 or higher). Efficient photopolymerization is also obtained with BP^{2-}. The quantum yields of polymerization are 700 for BP^+–TEA, 200 for BP^-–TEA, 65 for BP^- and 65 for BP^{2-} ([AA] = 1 M; [TEA] = 0.05 M) (see Table 1).

TABLE 1

Rates and quantum yields ϕ_m of polymerization of AA in the presence of different amines

Amine	$R_p \times 10^3$ ($M\ s^{-1}$)	ϕ_m
Triethylamine	1.65	400
Methyldiethanolamine	2.3	700
Triethanolamine	2.9	870

Initiator, BP^+; $I_0 = 3.8 \times 10^{15}$ photons cm^{-2} s^{-1}; [amine] = 0.05 M; [AA] = 0.7 M.

3.1.2. Role of I_0 and OD

The rate R_p of photopolymerization of AA is proportional to the square root of the incident light intensity I_0 (Fig. 2) and of the optical density OD (Fig. 3) according to the classical equation

$$R_p = \frac{k_p}{k_t^{0.5}} [M] (2.3 I_0 OD \phi_i)^{0.5}$$

where k_p and k_t are the propagation and termination rate constants, [M] is the monomer concentration and ϕ_i is the quantum yield of the initiation process.

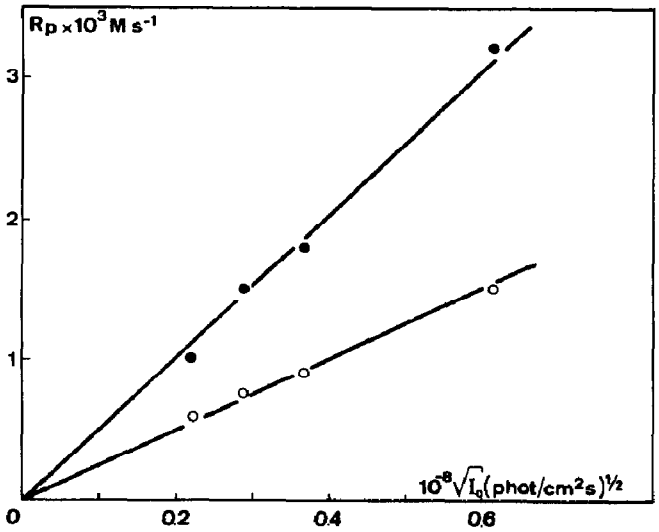


Fig. 2. Rate of polymerization *vs.* incident light intensity for aqueous solutions of AA: ○, 0.7 M AA; ●, 1.4 M AA. Initiator, BP^+; [TEA] = 0.05 M.

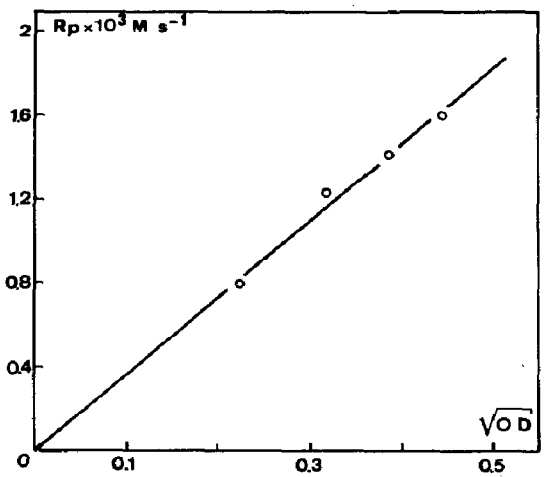


Fig. 3. Rate of polymerization of AA *vs.* optical density (initiator, BP^+; [TEA] = 0.05 M, [AA] = 0.7 M; $I_0 = 6.3 \times 10^{-6}$ einsteins l^{-1} s^{-1}).

3.1.3. Influence of the monomer concentration

The rate of polymerization of AA increases with its concentration (Fig. 4) and is proportional to $[M]^{\alpha}$. The coefficient α depends on the particular initiator–amine combination. In the case of BP^+–TEA $\alpha = 1$, whereas with BP^-–TEA $\alpha = 1.6$. The influence of the monomer concentration upon the photoinitiation efficiency of BP^- and BP^{2-} in the absence of amine is also shown in Fig. 4; $\alpha = 1.5$ in the case of BP^- and $\alpha = 1$ for BP^{2-}.

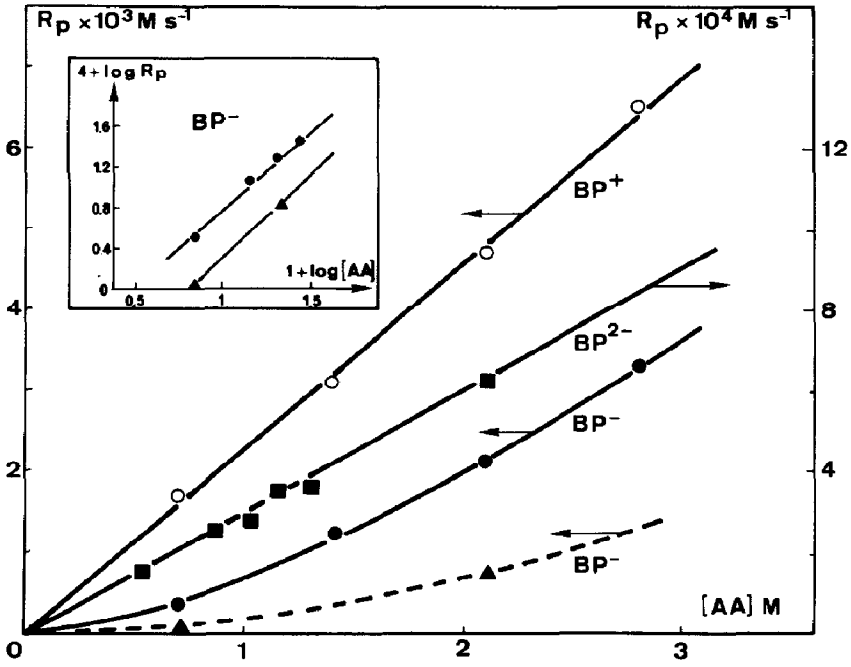


Fig. 4. Rate of polymerization *vs.* AA concentration: ○, BP^+; ●, BP^- ([TEA] = 0.05 M (broken line, BP^- without TEA)), $I_0 = 6.3 \times 10^{-6}$ einsteins l^{-1} s^{-1}; ■, BP^{2-}, $I_0 = 5 \times 10^{-5}$ einsteins l^{-1} s^{-1}. Inset: log–log plot of R_p *vs.* [M] for BP^-.

3.1.4. Influence of the amine

The rate of photopolymerization of AA in the presence of BP^+ is greatly increased upon addition of amines. The square root dependence of R_p on the amine concentration was clearly observed for TEA (Fig. 5) and also TEOH (Fig. 6). In the case of BP^- the influence of the amine depends drastically on its chemical structure: the influence of the amine is more pronounced in the presence of TEOH. The polymerization rate increases with TEA concentration, but for [TEA] > 0.05 M a plateau is reached (Fig. 5).

3.2. Laser study of $^3BP^{+*}$ and $^3BP^{-*}$

Addition of AA to an aqueous solution of BP^+ and BP^- induces a decrease in their triplet state lifetime (Fig. 7, insets A and B).

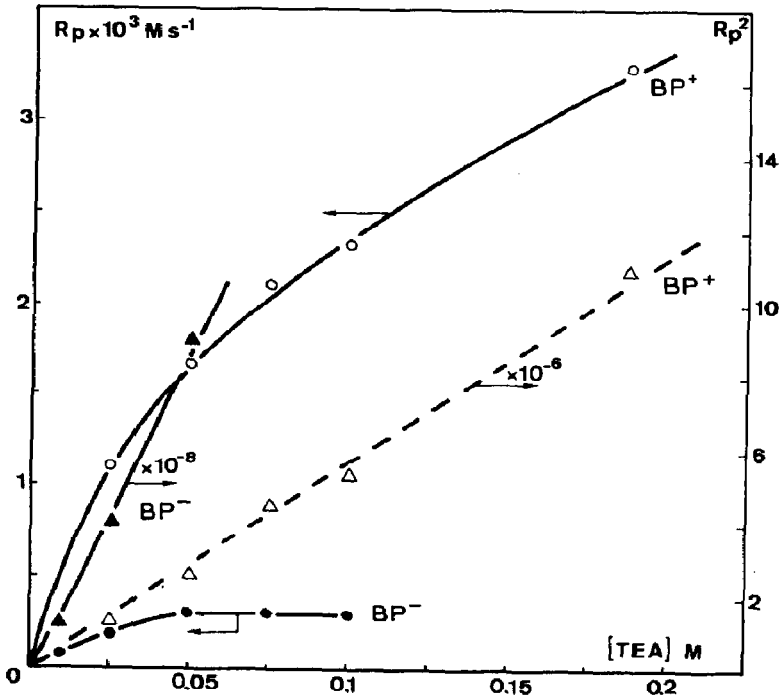


Fig. 5. Influence of the addition of TEA on the rate of polymerization of AA in the presence of BP^+ (○, △) and BP (●, ▲).

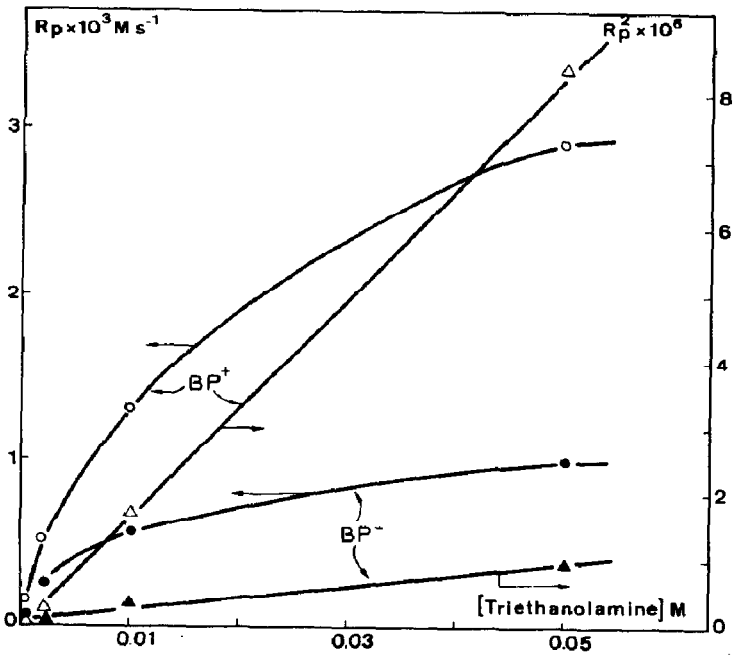


Fig. 6. Influence of the addition of TEOH on the rate of polymerization of AA in the presence of BP^+ (○, △) and BP^- (●, ▲); [AA] = 0.7 M.

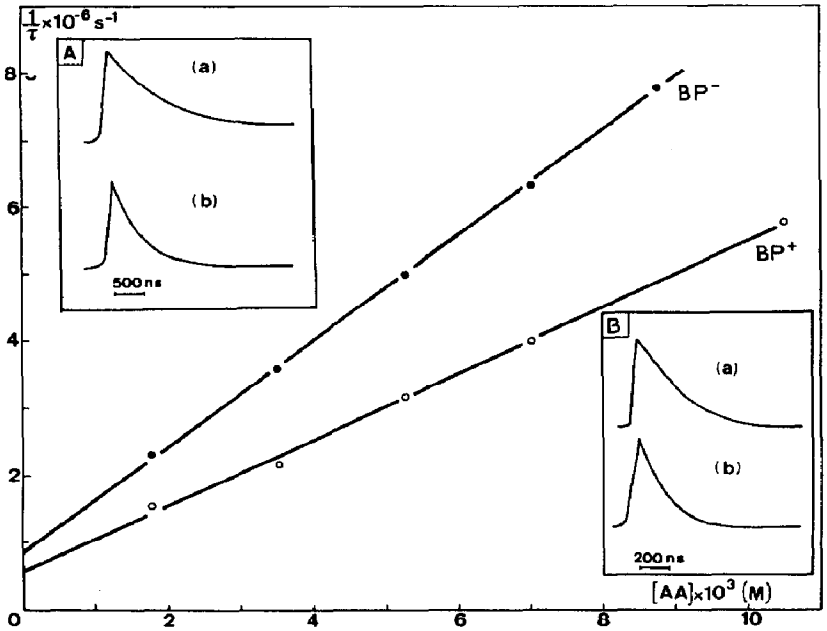
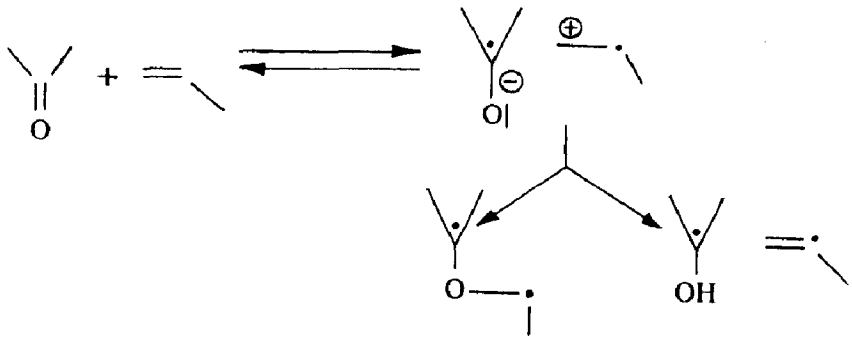


Fig. 7. Stern–Volmer plot of the reciprocal value of triplet state lifetime *vs.* AA concentration. Inset A: $^3BP^{-*}$ absorption (a) in the absence of AA and (b) in the presence of AA (1.8×10^{-3} M) at $\lambda = 525$ nm. Inset B: $^3BP^{+*}$ absorption in the presence of (a) 5×10^{-3} M AA and (b) 10^{-2} M AA at $\lambda = 525$ nm.

The quenching of $^3BP^{-*}$ and $^3BP^{+*}$ probably occurs by a physical process involving the triplet states of the benzophenones and AA since no residual absorption corresponding to the ketyl radical was detected. The same type of interaction has been observed for quenching of $^3BP^*$ by acrylic monomers [3, 8]. It presumably occurs through an electron transfer process [11] which is mainly followed by a back electron transfer and/or the formation of biradical; radicals derived from the ketyl and AA can also be imagined:



The rate constants for bimolecular quenching (Table 2) by AA, calculated by kinetic analysis (Stern–Volmer plot of Fig. 7), are 8.8×10^8 M^{-1} s^{-1} and 4.9×10^8 M^{-1} s^{-1} for BP^- and BP^+ respectively; these are higher than the constants for acrylates (10^7 - 10^8 M^{-1} s^{-1}) [5].

TABLE 2

Rate constants for quenching

	k_q [a] ($\times 10^8$ M^{-1} s^{-1})	k_e [b] ($\times 10^9$ M^{-1} s^{-1})	k_e [c] ($\times 10^9$ M^{-1} s^{-1})
BP^+	4.9	1.6	0.5
BP^-	8.8	1.2	1.1

[a] Quenching by monomer.
[b] Quenching by triethanolamine.
[c] Quenching by triethylamine.

Addition of TEA also shortens the transient lifetime of the triplet states of benzophenones but the usual residual absorption of the ketyl radical is observed simultaneously according to Scheme 1 (Fig. 8). In order to rule out any complications arising from the possible existence of an acid–base equilibrium in the presence of TEA (which can be regarded as a rather strong base), the experimental wavelength was chosen so that the extinction coefficients of the ketyl radical and of the anion radical were almost the same, as in the work on TEOH described in ref. 1. The rate constant for quenching of $^3BP^{-*}$ by TEA is equal to 1.1×10^9 M^{-1} s^{-1} and is comparable with that obtained for TEOH (1.2×10^9 M^{-1} s^{-1}).

The reciprocal optical density OD_∞^{-1} is proportional to $[TEA]^{-1}$,

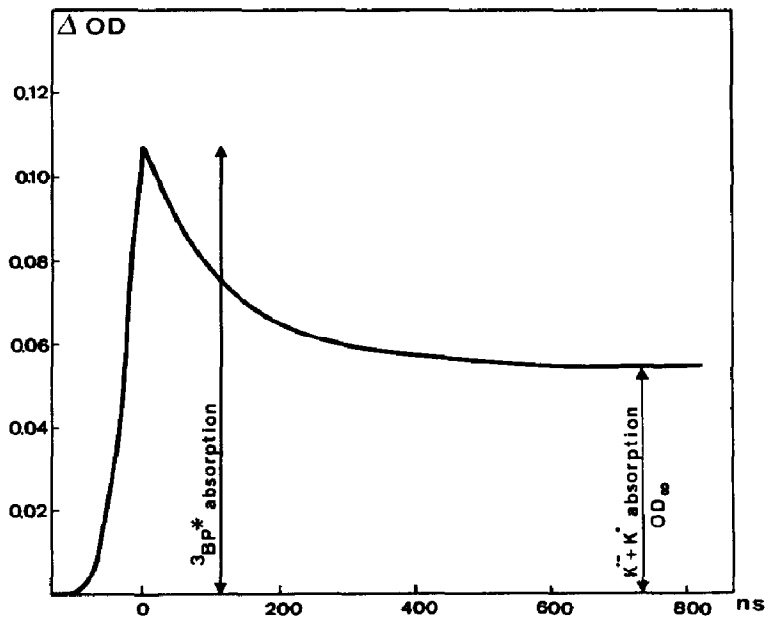


Fig. 8. Decay trace of $^3BP^{-*}$ observed at 485 nm in the presence of 7.4×10^{-3} M TEA.

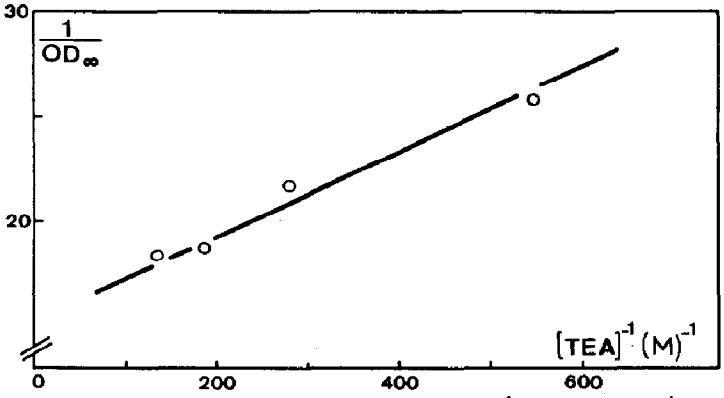


Fig. 9. Reciprocal optical density OD_∞^{-1} *vs.* $[TEA]^{-1}$ (initiator, BP^-; λ = 485 nm).

according to the equation

$$\frac{1}{OD_\infty} = \alpha\left(1 + \frac{k_0}{k_e}\frac{1}{[TEA]}\right)\frac{k_2}{k_1 + k_2}$$

proposed in ref. 9 (Fig. 9). This proves the consistency of the postulated quenching process with the experimental data (the value of k_0/k_e calculated from the slope is 0.02). Unfortunately, it has not been possible to find any isosbestic point in the transient spectra of BP^+. Throughout the range of wavelengths studied the oscillograms correspond to the superimposition of several transient absorptions: the decay of the triplet state and the formation and relaxation of both ketyl and ketyl anion radicals (as [TEA] is increased, OD_{max} approaches OD_∞ and exact analysis of the decay trace becomes impossible). Therefore, the kinetic analysis of the decay of $^3BP^+$ is rather inaccurate and the rate constant for quenching of the triplet state of BP^+ by TEA calculated in this way ($k_e = 5 \times 10^8$ M^{-1} s^{-1}) must be regarded as a rough approximation.

3.3. Flash study of $^3BP^{2-*}$

The kinetic curves of BP^{2-} photolysis (Fig. 10, inset) show two decay processes occurring with very different lifetimes. Since the ratio of the optical density at the maximum and at the end of the decay curve is wavelength dependent, two transients are involved. The long-lived transient is attributed to the ketyl radical (the corresponding optical density is increased upon addition of methanol and the transient decays according to second-order kinetics). On the contrary, the short-lived transient decays according to pseudo-first-order kinetics and disappears completely in the presence of methanol. The transient triplet absorption spectra of both $^3BP^{2-*}$ (λ_{max} = 530 nm) and its ketyl radical (λ_{max} = 550 nm) are very similar to the spectrum of ground state benzophenone.

The triplet lifetime of $^3BP^{2-}$ was determined to be 24 μs. Since the lifetime of the flash is of the same order of magnitude, the constant for quenching by AA was calculated from a Stern–Volmer treatment of $1/OD_K$· *vs.* [AA] (Fig. 10). This process can be described by the following scheme:

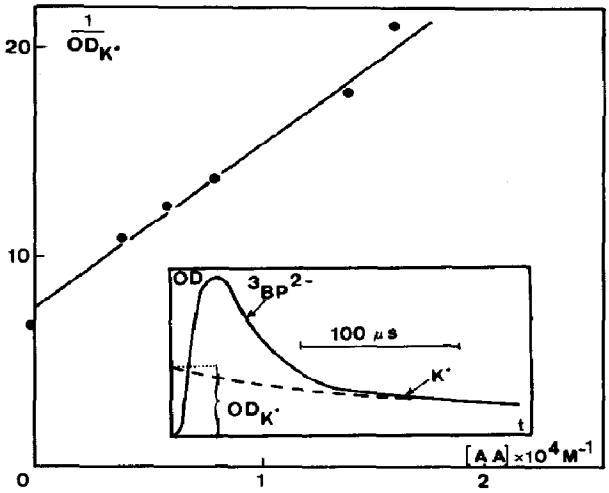
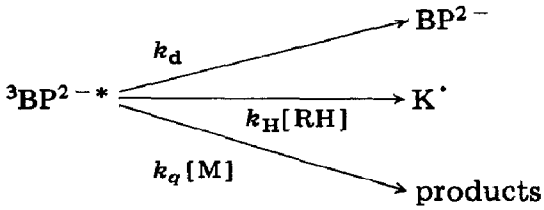


Fig. 10. Stern–Volmer plot of the reciprocal optical density of the ketyl radical of BP^{2-} *vs.* $[AA]^{-1}$. Inset: decay trace of excited BP^{2-} in water at λ = 500 nm.



The efficiencies of ketyl radical formation in the presence of AA ($\rho_{K_0^{\cdot}}$) and in the absence of AA ($\rho_{K^{\cdot}}$) are

$$\rho_{K^{\cdot}} = \frac{k_H[RH]}{k_d + k_H[RH] + k_q[M]}$$

and

$$\rho_{K_0^{\cdot}} = \frac{k_H[RH]}{k_d + k_H[RH]}$$

The ratio of the initial optical densities of the ketyl radicals can be written as

$$\frac{OD_{K_0^{\cdot}}}{OD_{K^{\cdot}}} = \frac{\rho_{K_0^{\cdot}}}{\rho_{K^{\cdot}}} = 1 + \frac{k_q[AA]}{k_d + k_H[RH]} = 1 + k_q{}^3\tau[AA]$$

The plot in Fig. 10 agrees with this equation and leads to a quenching rate constant for $^3BP^{2-*}$ of 4.2×10^8 M^{-1} s^{-1}. Thus, in a molar aqueous solution of AA, $^3BP^{2-*}$ decays mainly by quenching by the AA.

3.4. Model of polymerization

From the results obtained through laser spectroscopy, a kinetic model for the polymerization photoinitiation can be built up; the following relation holds:

$$R_i = 2.3\mathrm{OD}I_0\phi_{ST}\ \frac{k_e[A]}{k_e[A] + k_0 + k_q[M]}\ \phi_A\beta = 2.3\mathrm{OD}I_0\phi_i$$

and

$$R_p \propto [M]R_i^{0.5} \propto [M]\mathrm{OD}^{0.5}I_0^{0.5}\phi_i^{0.5}$$

with

$$\phi_A = \frac{k_2}{k_1 + k_2}$$

$$\beta = \frac{k_{RM}[M]}{\Sigma k} = \rho[M]$$

As expected from the experimental values of the rate constants, in the case of the systems BP^+–TEA and BP^+–TEOH it is easily calculated that the following relationships should be valid over the range of concentrations used:

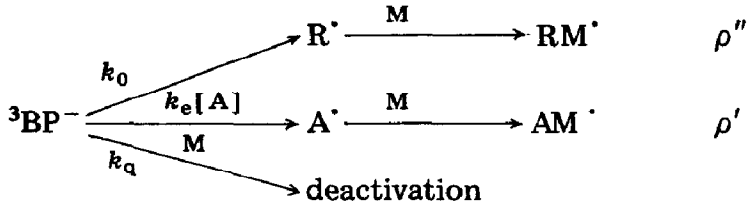
$$R_p = K[M][A]^{0.5}$$

because

$$\phi_i \propto K'\ \frac{k_e[A]}{k_q[M]}\ [M] \propto K''[A]$$

The plots of Figs. 4 - 6 indicate that there is satisfactory agreement with the predicted behaviour; hence it is concluded that BP^+ behaves in the same way as the oil-soluble homologue BP.

This model is probably inadequate in the case of BP^- and BP^{2-} since it does not take into account the fact that polymerization readily occurs in the absence of amine. In this case, it could be assumed that the initiation occurs directly from $^3BP^{-*}$ and $^3BP^{2-*}$. In fact, recent results obtained through laser spectroscopy with BP^- show that photoreduction takes place in water even in the absence of any hydrogen donor [1]. The same is true in the case of BP^{2-} (Fig. 10, inset). No clear assignment of the nature of the radicals formed or their mechanism of formation can be proposed as yet. A thorough study of the laser photolysis of BP^- in H_2O and D_2O led us to the conclusion that the yield of photoreduction and the rate constants k_0, k_{sq} (self-quenching) and k_{TT} (triplet–triplet annihilation) are almost insensitive to a one order of magnitude change in concentration in these solvents and to an increase in the laser dose absorbed; thus photoreduction by water seems rather unlikely. An upper limit k_0 for the radical generation has been estimated to be 10^5 - 10^6 s^{-1}. This process remains a minor pathway of deactivation which becomes completely inoperative in the presence of monomer and amine and as a consequence does not contribute to the initiation process. The following scheme is proposed:



The following relationship holds:

$$R_p = K[M]\phi_i^{0.5}$$

with

$$\phi_i \propto \frac{1}{k_0 + k_q[M] + k_e[A]} (k_e[A]\phi_A\rho' + k_0\rho'')$$

Since the ratio of the R_p in the presence and in the absence of amine is about 3, the corresponding initiation efficiencies are in the ratio of about 8:1. This suggests that the direct initiation plays a minor role in the photoinitiation step. Thus, by introducing the experimental values of the different constants into the above relationship, it should still reduce to

$$R_p \propto [M][A]^{0.5}$$

for BP^- and BP^{2-}; in practice, the expression does not fit the experimental results well (especially as regards the monomer dependence). Only very rough agreement is observed for $R_p = f[A]$ with the system BP^-–TEOH. A similar relationship holds for TEA over the same amine concentration range (below 0.05 M); however, at higher amine concentrations, secondary reactions presumably occur with amine-derived radicals.

An anomalous monomer dependence has been already observed in AA radical polymerization initiated by various systems [14 - 17]; *e.g.* in the light-induced polymerization of an aqueous solution of AA and eosine the mediation of a complex between the photoinitiator and the monomer was suggested two decades ago [14, 15] in order to explain a non-linear dependence of R_p on [M], but neither an accurate kinetic treatment nor the structure of the complex have been proposed so far. However, it is obvious that the rate of generation of an intermediate complex such as BP···M should depend on [M], and the yield of conversion of this complex into initiating radicals must therefore strongly depend on [M], as will be discussed below. However, no obvious explanation can be invoked to account for the different behaviour of BP^-, BP^{2-} and BP^+ towards monomer and solvent.

Thus, Scheme 2 might satisfactorily fit the experimental results. In addition to the $^3BP^-$–amine interaction (CT_1), monomer quenching of the triplet state of BP^- and BP^{2-} results in the generation of a charge transfer complex CT_2 which either undergoes proton transfer or attachment of the two radical ions (yielding species B) or leads (through a triplet mechanism [13]) to an electron transfer reaction with an amine (forming a CT complex

(II) BP^- if $\rho'[M] \neq$ const, *i.e.* if deactivation of B competes with initiation.

(III) BP^+ if $A_3 = 0$, which means that initiation is inefficient through monomer quenching ($k_d \gg k_b$).

Using this approach, the direct initiation in the absence of amine might be due to the generation of biradicals through monomer quenching, the alkyl end being the active species. In this case, the ketyl chain end must ultimately terminate the growing chains. Thus, one can approximatively estimate the ratio of the R_p of BP^+ and BP^-:

$$\omega = \frac{R_p(BP^+)}{R_p(BP^-)} \approx \frac{KM[A]^{0.5}}{K'M^{1.5}[A]^{0.5}} = \frac{K}{K'}[M]^{-0.5}$$

With [M] = 0.7 M and [M] = 2.1 M, ω is experimentally measured to be 4.4 and 2.1 respectively; thus K/K' is equal to 3.7 and 3 respectively. The proportionality factors are a function of $k_p/k_t^{0.5}$ and of the rate constants of all the processes occurring during the photoinitiation and including the interaction of the complex with the monomer. With regard to the primary processes involved in the excited states, it can be concluded that the difference in reactivity between BP^{2-}, BP^- and BP^+ originates from the relative efficiencies of routes 1, 22 and 3 (Scheme 2), which are related to measurable parameters (k_e, k_q) and inaccessible data (k_e', k_b, ϕ_A, $\phi_{A'}$). Such a difference has recently been noted in other studies of photopolymerizable systems: sodium dodecylsulphate micelles of MMA in water [18] and AOT micelles of AA in decane [19]. Other detrimental processes of the deactivation involving the ketyl or the ketyl anion radical cannot be completely ruled out.

4. Conclusions

This study reports a careful investigation of the triplet state processes of novel water-soluble benzophenone derivatives. The usual electron transfer processes occur in the presence of amine and monomer: at first it appeared that the anionic and cationic characters of these compounds play no detectable role in the dynamics of the excited states in homogeneous solutions of AA in water, although steady state experiments suggest that the interactions between triplet states and monomer molecules differ significantly from the behaviour of benzophenone itself. However, sharp differences are observed in their efficiencies as photoinitiators of polymerization, and chemical effects as well as subsequent photophysical and photochemical effects must be invoked to explain this type of behaviour. Lastly, it must be pointed out that, at the moment, ionic benzophenones are potentially the most efficient and promising initiators for photopolymerization of water-based systems. Other ionic benzophenone derivatives follow the same trend.

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