Short Communication

Inefficiency of some aryl ketones in sensitizing biacetyl phosphorescence in aqueous solution

G. FAVARO

Istituto di Chimica Fisica, Università di Perugia, 06100 Perugia (Italy)

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In the course of a study on the efficiency of aryl ketones as triplet donors in aqueous solvent [1, 2], the *p*-amino (4-NH$_2$-Bp) and *p*-hydroxy (4-OH-Bp) benzophenones have been investigated. These compounds, owing to the characteristics of their absorption spectrum and the changes that it undergoes due to pH variations, could be expected to act as good sensitizers, using a large range of exciting wavelengths, depending on the pH value of the solution, and therefore be coupled with different acceptors.

However, experiments on sensitization of biacetyl phosphorescence, a technique well improved in previous works [1 - 4], gave no positive results for either compounds over the whole pH interval explored (1 - 10).

Since these compounds show phosphorescence emission in rigid matrix at low temperature at every pH value, the lack of sensitized phosphorescence can be attributed to some competitive process involving triplet excited molecules of the donor or of the acceptor.

We attempted to discover what role, if any, a back reaction of biacetyl triplet with the ground state aryl ketones could play in the inhibition of the sensitization process. The occurrence of quenching of biacetyl phosphorescence by amino and hydroxy benzophenones, observed by exciting biacetyl directly, could justify the absence of sensitizing power of these compounds, at least in part. Moreover, this behaviour suggests that self-quenching may also play an important role in deactivating the triplet states of substituted benzophenones in aqueous solution.

Experimental

Reagent grade *p*-amino and *p*-hydroxy benzophenones were purified by standard procedures. Britton buffers, containing 3% by volume of ethanol for solubility requirements, were used as solvents from pH 10 to 2. HClO$_4$ solutions were used for lower pH values.

Absorption spectra were performed on a Unicam SP500/2 single beam spectrophotometer. Phosphorescence spectra were recorded both at room

and liquid nitrogen temperature on a Hitachi/Perkin-Elmer MPF-3 spectro-fluorimeter, using an accessory for phosphorescence measurements at low temperature.

The pK values were determined at room temperature ($22° \pm 2$ °C) by u.v. absorption measurements at wavelengths where the basic form only absorbs (375 nm for 4-NH$_2$-Bp and 390 nm for 4-O$^-$-Bp). The pH intervals of measurements were 5 - 2 for the amino and 9 - 7 for the hydroxy-derivative, at constant ionic strength ($\mu = 0.01$) and 3% by volume of ethanol. A Sargent PXB pH-meter with a glass electrode was employed.

Quenching experiments of biacetyl phosphorescence were run at room temperature with constant biacetyl concentration ($4.5 \times 10^{-2} M$), varying the concentration of the quenchers in the range 2×10^{-6} - $4 \times 10^{-5} M$, in de-aerated solution. Linear Stern–Volmer plots were obtained, following the equation:

$$P°/P = 1 + k_t \tau [\text{Bp}] \tag{1}$$

where $P°$ and P are the phosphorescence intensities (525 nm) of the directly excited (420 nm) biacetyl in the absence of Bp and at varying Bp concentrations, respectively. k_t is the quenching constant and τ is the triplet lifetime of biacetyl.

Owing to the photochemical instability of biacetyl and 4-NH$_2$-Bp in acidic medium, the solutions were stored in the dark and the measurements performed as soon as possible. The reproducibility error was within 15%.

No quenching was observed for 4-OH-Bp in neutral or acidic solution to $2 \times 10^{-4} M$, practically the saturation value.

Results and Discussion

Absorption spectra in water, reported in Fig. 1 for the acidic and basic forms, are similar to those previously obtained in isopropanol [5], showing an intense CT band for the bases and a higher energy absorption for the acids. The n,π^* transition is evident for 4-NH$_3^+$-Bp only, but it can be submerged by the more intense π,π^* one for the hydroxy-derivative. The energies for the lowest transitions, together with the extinction coefficients, are shown in Table 1.

The pK values, shown in Table 1, determined spectrophotometrically, are rather different from those reported in the literature ($\Delta pK = 1.5$) [5, 6], probably due to the different solvent used.

Phosphorescence spectra were recorded for both compounds in a large pH interval (pH 0 - H$_o$ −5) and have in common with benzophenone [7] the characteristic of showing more emissions than those expected from the acid–base equilibria and of being dependent on the exciting wavelength at certain pH values. Their attribution to a specific molecular form in Table 1 is tentative, since some phosphorescence may occur from specific conformations trapped in the 77 K glasses. In Fig. 2, the emission spectra from
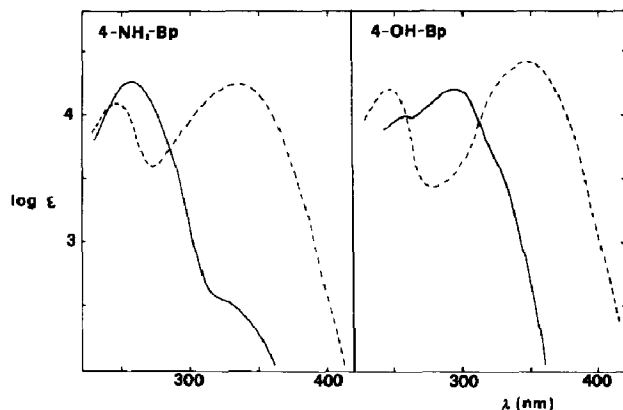
Fig. 1. Absorption spectra in 97:3 (v/v) water–ethanol solutions of p-amino and p-hydroxy benzophenones in their acidic (——) and basic (·····) forms.

TABLE 1

Energies of the lowest singlet and triplet levels and pK values for benzophenone derivatives in aqueous solution.

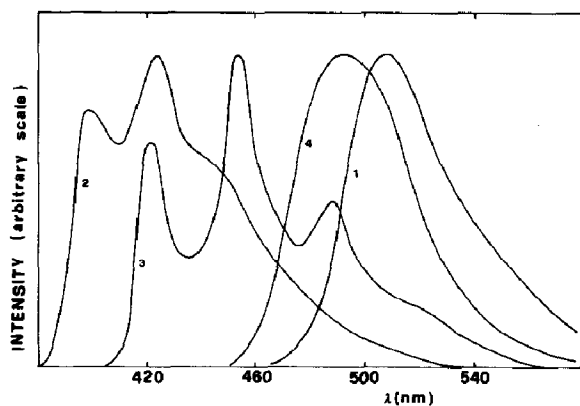| Molecular species	$\bar{\nu}_{S_1}$ (log ϵ) $\times 10^3$(cm^{-1})	$\bar{\nu}_{T_1}$ $\times 10^3$(cm^{-1})	pK
4-NH$_2$-Bp	29.85 (4.23)	20.80	
4 NH$_3^+$-Bp	30.30 (2.51)	25.05	2.0 (0.5) [5]
4-O$^-$-Bp	28.70 (4.21)	21.30	
4-OH-Bp	33.90 (4.41)	23.80	8.0 (6.5) [6]

Fig. 2. Uncorrected phosphorescence spectra of p-amino benzophenone in water matrices of different acidities at 77 K. 1, pH 5; 2, pH 0; 3, H$_o$ - 4; 4, H$_o$ - 5.5.

4-NH$_2$-Bp are shown. Low energy structureless emission (1) derives from a CT excited state: its duration is shorter than that of the more structured high energy π,π^* emission (2) which appears below pH 2.5. Only near H$_o$ —4

does the spectrum of 4-NH$_2$-Bp assume the characteristic feature of a n,π^* transition (3), whilst this never occurs for 4-OH-Bp. Emission (4) belongs to the protonated carbonyl molecule and is the only emission present below H_0 —5.5, a value somewhat higher than that corresponding to the pK (—6.4) [8], indicating probably a more basic triplet state. The occurrence of the emissions (2) and (3) and their dependence on the acidity of the matrix can find an explanation analogous to that given for benzophenone itself [7].

However, these emissions show that the triplet is populated through excitation at each pH value and that exothermic energy transfer to biacetyl ($E_T = 19.80 \times 10^3$ cm^{-1}) could be possible, contrary to the experimental findings.

The quenching constants for biacetyl phosphorescence, k_t, determined from the Stern–Volmer plots and the triplet lifetime of biacetyl (6 $\times$ 10^{-5} s), are compared in Table 2 with those previously obtained for the neutral forms in benzene solution [4]. The pH values at which they were measured have been chosen on the basis of the pK values. Owing to the thermal instability of biacetyl at low pH and to avoid a change in the ionic strength of the solutions, the k_t value for the acid 4-NH$_3^+$-Bp was extrapolated from measurements at pH $\geqslant$ 2, utilizing the equation:

$$P^o/P = 1 + \tau[\text{Bp}]\{k_t^a + \alpha(k_t^b - k_t^a)\} \tag{2}$$

This equation accounts for the effect of the dissociation (α), relating the quenching constant for the base (k_t^b) and for the acid (k_t^a) to the observed intensity emission ratio (P^o/P). The slopes of the Stern–Volmer plots, obtained at different pH values, plotted against α, give a straight line with intercept τk_t^a and slope $\tau(k_t^b - k_t^a)$.

Since benzophenone does not quench biacetyl phosphorescence in aqueous solution [1], the behaviour of these two derivatives can be interpreted as due to a specific interaction between excited biacetyl and the functional group in the aromatic ring. An energy transfer mechanism can be ruled out, considering that biacetyl triplet is lower than that of aryl ketones.

The quenching of biacetyl fluorescence and phosphorescence by amines and phenols was investigated by Turro et al. [9 - 12], and was interpreted as

TABLE 2

Quenching constants of biacetyl phosphorescence by benzophenone derivatives in aqueous and organic solvent.

Molecular species	$k_t \times 10^9$ (M^{-1} s^{-1})	
	Aqueous solvent	Benzene
4-NH$_2$-Bp	6.0 ± 0.2	0.16 [4]
4-NH$_3^+$-Bp	0.8 ± 0.1	
4-O$^-$-Bp	2.4 ± 0.2	
4-OH-Bp	<0.01	0.02 [4]

a chemical process involving an electron transfer mechanism for the amines and a reversible hydrogen abstraction process for the phenols. The increase in k_t for 4-NH$_2$-Bp, going from benzene to water, where its value is diffusion controlled, is in agreement with the proposed mechanism since an increase in the dielectric constant of the solvent should favour the formation of a CT complex more polar than the separate species. On the other hand, the absence of observable quenching for 4-OH-Bp in water is not unexpected, since hydrogen bond formation with the solvent hinders the hydrogen transfer from the OH group to the excited biacetyl. Lack of quenching of biacetyl phosphorescence by phenols was in fact found in dioxane, a solvent with a low dielectric constant but a high hydrogen bonding power [10].

As regards the charged species, the k_t values are fairly high, approaching the diffusional value for 4-O$^-$-Bp. In this case the quenching mechanism probably implies an electron transfer from the anion to biacetyl. Inorganic anions have also in fact been found to quench biacetyl phosphorescence by a charge transfer mechanism [13].

From these results a reasonable interpretation can be proposed for the lack of phosphorescence sensitization of biacetyl using 4-NH$_2$- and 4-OH-Bp as donors, although population of the donor triplets and energy requirements are fulfilled. It is conceivable that a back quenching of biacetyl triplet, when excited by energy transfer from the aryl ketones, occurs in a rate-determining manner before the emission of the sensitized phosphorescence. Moreover, such an efficient quenching between the excited carbonyl and the functional groups here considered, suggests also that a very efficient self-quenching could play an important role, as was experimentally observed in benzene [4]. For 4-OH-Bp, where no quenching has been observed, vibrational deactivation through hydrogen bonding with the solvent probably competes with any other process.

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