Photochemical reactivity of *para*-aminobenzophenone in polar and non-polar solvents

Nagwa Ghoneim, Alberto Monbelli, Denis Pilloud, Paul Suppan

Institute of Physical Chemistry of the University of Fribourg, CH-1700 Fribourg, Switzerland

Abstract

In non-polar cyclohexane solution, *para*-aminobenzophenone (PAB) has a triplet yield of 0.82 and a reaction quantum yield of 0.21 towards hydrogen abstraction. In polar *N,N*-dimethylformamide (DMF), the triplet yield is 0.1, but the reaction quantum yield is below 10^{-5}; other reactive benzophenones are photoreduced efficiently in the same solvent. This difference in photoreactivity is related to the nature of the lowest triplet excited state, which is n–π^* (reactive) in non-polar solvents but of "charge transfer" (CT) type in polar media. In polar, protic solvents, such as ethanol, the triplet yield is very low as a result of quenching of the CT singlet excited state by proton transfer.

Keywords: 4-Aminobenzophenone or methanone (4-aminophenyl-phenyl), CA reg. 1137-41-3; Photoreduction; Solvent effect; Charge transfer states

1. Introduction

para-Aminobenzophenone (PAB) is photoreduced efficiently in non-polar cyclohexane, but is quite unreactive in polar, protic ethanol. This remarkable solvent dependence has become a textbook example of the influence of excited state charge distribution on photochemical reactivity. In the case of PAB, it has been explained by a switching of the excited states, such that the lowest triplet level is a reactive n–π^* state in non-polar solvents, but a "charge transfer" (CT) state in polar solvents [1]. The primary process during photoreduction involves hydrogen atom abstraction by the excited carbonyl compound (e.g. PAB) from a hydrogen donor substrate (which can be the solvent); this is favourable when the carbonyl oxygen atom is electron deficient as is the case in the n–π^* state. However, the carbonyl group receives a high negative charge in the CT state, since an electronic charge of 0.8 is transferred from the amino-substituted aromatic ring to the carbonyl acceptor group.

However, there may be a different explanation for the low reactivity of PAB in ethanol. It has been pointed out that, in this solvent, the triplet yield is extremely low (less than 10^{-5}), and this alone could explain its unreactivity [2]. The precise reason for this low triplet yield has not been established firmly, but it is probably related to the protic nature of the solvent rather than to its dielectric polarity, since the triplet yield is high in acetonitrile.

The quenching action of protic solvents, such as ethanol, therefore leaves open the question of the chemical reactivity of the CT triplet state, when it is formed in reasonably high yield in some polar, non-protic solvents. The assessment of the intrinsic reactivity of the CT triplet state towards hydrogen abstraction is the object of this paper.

Acetonitrile (MeCN) is not suitable for this purpose, since it is a very poor hydrogen donor [3]. In this solvent, even benzophenone is photoreduced with very low efficiency, the second-order rate constant being of the order of 130 M^{-1} s^{-1}.

N,N-Dimethylformamide (DMF) has therefore been chosen as the polar, non-protic hydrogen donor solvent. The triplet yield and reaction quantum yield of PAB were measured in this solvent and solvent mixtures, and the unreactivity of the CT triplet state towards hydrogen abstraction was confirmed.

2. Experimental details

The steady state reaction quantum yields were determined with reference to the anthraquinone actinometer. Irradiations were carried out using a 100 W high pressure Hg arc/monochromator combination for precise quantum yield measurements, or through filters for limiting quantum yields in the case of very low photoreactivity: filter for cut-off at 400 nm, 75 g NaNO$_2$ in 100 ml water (path length, 1 cm); filter for

cut-off at 350 nm, 2 M KNO_3 in water (path length, 2 cm). The laser flash photolysis instrument is the same as that used in Ref. [4].

2.1. Samples

All solvents were of FLUKA UV grade and were used as received. Anthraquinone, naphthalene (NH) and PAB were purified by double sublimation. Benzophenone (BP) and 4,4'-dimethoxybenzophenone (DMBP) were purified by recrystallization. All solutions were degassed by the freeze–pump–thaw–shake procedure.

3. Results and discussion

3.1. Photochemical reactivity in cyclohexane (CH) and DMF

The photochemical reactivity of PAB in these solvents is compared with that of DMBP which is a highly photoreactive molecule with well-characterized n–π^* lowest triplet states

Table 1
Quantum yields of photoreduction of PAB and DMBP in various degassed solvents

	Solvent					
	Benzene	CH	Toluene	THF	DMF	EtOH
PAB	2×10^{-2}	0.21	0.1	0.11	$<10^{-5}$	$<10^{-5}$
DMBP		1.7			0.2	0.5

CH, cyclohexane; THF, tetrahydrofuran; DMF, N,N-dimethylformamide; EtOH, ethanol.

in all solvents. Table 1 shows the quantum yields of photoreduction of DMBP, which are high in both solvents, whereas there is a marked difference in the case of PAB; while the high reactivity of PAB in CH is confirmed in this work, PAB appears to be photostable in the polar solvent DMF which is clearly a good hydrogen donor.

3.2. Reactivity in solvent mixtures

Fig. 1 shows the variation of the reaction quantum yield of PAB in mixtures of diethylether and DMF (a) and tetrahydrofuran (THF) and ethanol (EtOH) (b) as a function of the polar solvent mole fraction. These curves are characteristic of the process of preferential solvation known as dielectric enrichment [5], and it is readily seen that they are very similar for the polar, non-protic solvent DMF and the polar, protic solvent EtOH. It is therefore clear that the quenching action results, in both cases, from the increasing population of the CT states of PAB with increasing polarity of the solvent mixtures, irrespective of the triplet yields (see below).
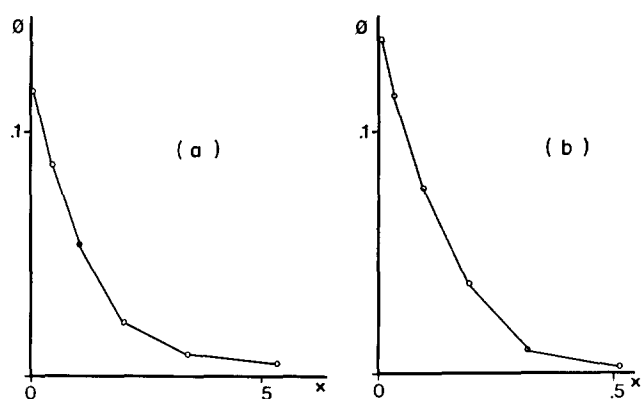

Fig. 1. Quantum yields of photoreduction of 4-aminobenzophenone in mixtures of diethylether and DMF (a) and THF and EtOH (b).

3.3. Triplet yields of PAB in CH and DMF

The triplet yields were determined by laser flash photolysis, using NH as the energy acceptor probe. This method has been described previously [4], and it is useful in principle for all molecules which have a higher triplet state than that of NH, at 2.13 μm.

When a solution of PAB in CH or DMF is irradiated with a 355 nm laser pulse of 25 ns duration in the presence of 5×10^{-2} M NH, energy transfer from ^{3}PAB to give ^{3}NH is practically quantitative. The initial absorbance of ^{3}NH at 413 nm gives a measurement of the donor's triplet yield, calibration being provided by a solution of BP and NH of the same absorbance at 355 nm. The results are shown in Table 2.

The triplet yield of PAB is very high in CH, close to 0.1 in DMF, but too low to measure in EtOH.

Table 2
Triplet yields of PAB in various degassed solvents

	Benzene	CH	DMF	EtOH
ϕ_T	0.67	0.82	0.1	$<10^{-5}$

The fact that triplet excited NH is formed shows that energy transfer takes place, so that the energy of T_1 of PAB in MeCN or DMF must be higher than that of T_1 of NH. The observation of phosphorescence in low temperature rigid matrices is in agreement with this assignment, but leaves open the question of solvent effects on the relative state energies in room temperature liquids. The precise triplet state energies of PAB in fluid DMF, MeCN and, in particular, EtOH have not been established, but the observation of energy transfer clearly shows that they are higher than that of NH in non-protic solvents. In fluid alcohol solvents, the triplet yield is zero, due to quenching by protonation of the S_1(CT) singlet state; the energy of T_1 cannot be established in this case.

3.4. Triplet yields in solvent mixtures

Fig. 2 shows the variation of the triplet yield of PAB in mixtures of diethylether and DMF and THF and EtOH. These
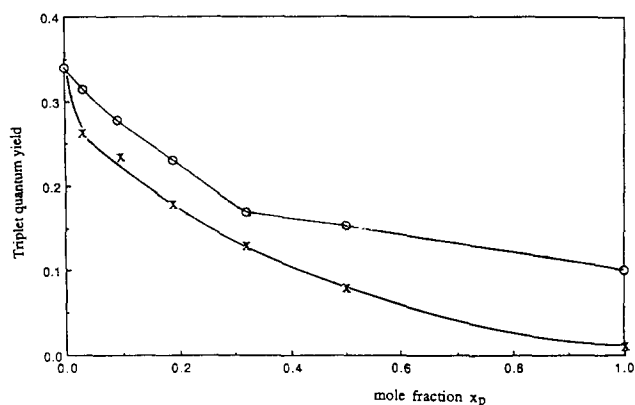
Fig. 2. Triplet yields of 4-aminobenzophenone in solvent mixtures: O, diethylether and DMF; ×, THF and EtOH.
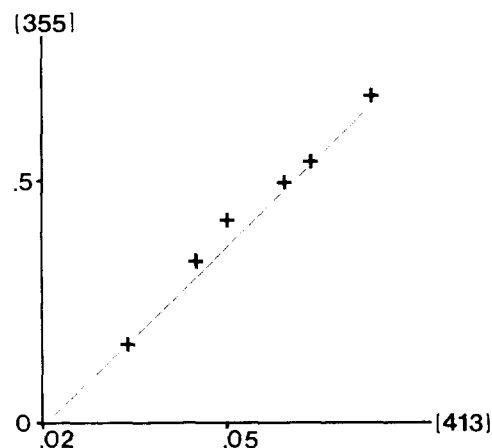

Fig. 3. Triplet–triplet absorbance of naphthalene in the presence of 4-aminobenzophenone at concentrations between 1.6×10^{-4} and 6×10^{-4} M. Abscissa, absorbance of triplet naphthalene at 413 nm. Ordinate, absorbance of 4-aminobenzophenone at 355 nm (excitation wavelength). Solvent, MeCN.

should be compared and contrasted with the reaction quantum yields shown in Fig. 1 for the same solvent mixtures. The slopes of the triplet yield functions are less pronounced and become nearly linear when the polar solvent mole fraction reaches about 0.3. In both cases, there is a decrease in the triplet yield with increasing polar solvent concentration, but this effect is quite small with the non-protic solvent DMF compared with the protic solvent EtOH. The decrease in the triplet yield alone cannot explain the decrease in the quantum yield of photoreduction, and it is clear that the CT state, when formed, is intrinsically unreactive.

3.5. Effect of PAB concentration on photoreduction and triplet formation quantum yields

In the PAB concentration range 1.6×10^{-4} to 6×10^{-4} M, both the photoreduction quantum yields in CH and the triplet yields measured in MeCN are independent of concentration. This contrasts with the conclusions of Ref. [2a], but it should be noted that, in Ref. [2a], much higher PAB concentrations were used; in addition, the concentrations of the triplet energy acceptors (trans-stilbene) were of the same order, around 2×10^{-3} to 5×10^{-3} M (compared with our NH concentration of 5×10^{-2} M). When the PAB concentration is high, self-quenching of the triplet becomes important, and this reduces the observed quantum yield of photoreduction. The proper definition of this quantum yield should be the extrapolation to zero concentration, and we find that below about 5×10^{-4} M PAB in CH this limit is practically reached.

We have also measured the triplet yield of PAB in MeCN within the concentration range mentioned above, and it is found that this is independent of concentration, as shown by the linear plot of the absorbance of the NH triplet vs. PAB concentration (Fig. 3). When the triplet energy acceptor (NH) concentration is increased from 5×10^{-2} M to 10^{-1} M, the NH triplet absorbance remains unchanged, providing clear evidence that, at these high acceptor concentrations, energy transfer from triplet PAB to NH is practically quantitative. With the much lower trans-stilbene concentrations used in Ref. [2a], the triplet yield will appear to depend on

the acceptor concentration. A proper measurement of the triplet yield should be the extrapolation to infinite quencher concentration; here we find that with NH concentrations above 5×10^{-2} M this condition is practically reached.

3.6. Triplet absorption spectra and lifetimes of PAB

Laser flash photolysis of PAB in MeCN and DMF shows triplet–triplet (T–T) absorption with a maximum around 465 nm. In BP, the first maximum of the T–T transitions is found around 540 nm, but in PAB the ordering of the triplet states in polar solvents is quite different since the lowest state is ^{3}CT instead of ^{3}n–π^*.

The lifetime of the triplet state of PAB depends on the ground state concentration, being about 3.6 μs at $[PAB] = 10^{-4}$ M; the decay of the triplet state results largely from concentration quenching. In CH solvent, only the characteristic second-order decay of the ketyl radical is observed.

3.7. Photophysics of PAB in different solvents

The relative positions of the lower excited states of PAB may provide an explanation of the differences in the triplet yields. In non-polar CH, spectroscopic evidence shows that the first singlet level S_1 and the first triplet T_1 are of n–π^* type, as in DMBP and BP itself [6]. In the latter molecule, there is a low-lying second triplet state T_2 of $\pi \rightarrow \pi^*$ type below S_1(n–π^*), which is responsible for the fast intersystem crossing and thereby for the high triplet yield (Fig. 4(a)) [9]. A similar arrangement of n–π^* and $\pi \rightarrow \pi^*$ excited states is kept in PAB in CH, because the new CT states (which do not exist in BP) remain at higher energies (Fig. 4).

In a highly polar solvent such as DMF, solvation of the CT states brings these below the n–π^* levels. This situation results in a lower rate of intersystem crossing, the spin-forbidden transition ^{1}CT $\rightarrow$ ^{3}CT being less allowed than a ^{1}(n–
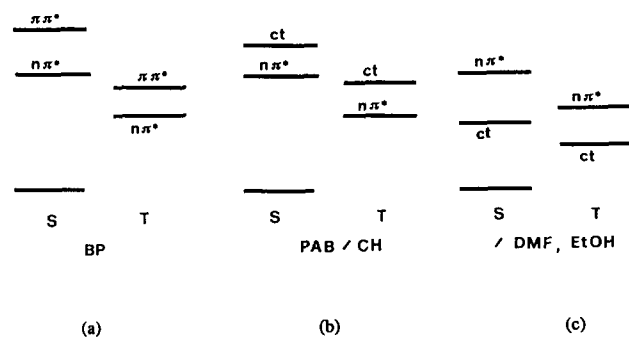
Fig. 4. Energy levels of benzophenone and 4-aminobenzophenone in different solvents.

$\pi^*) \to {}^3(\pi \to \pi^*)$ crossing; hence the lower triplet yield of around 0.1 (Fig. 4(c)).

In the case of PAB in EtOH, the triplet yield is zero, and this points to a different mechanism which involves the quenching of the CT singlet excited state by proton transfer from the solvent. This can be demonstrated for the similar molecule 4-aminophthalimide (4AP) by observation of the quenching of its fluorescence in protic solvents and in acidic solutions [8]. The intramolecular counterpart of this proton transfer reaction is well known to be responsible for the high photostability of 2-hydroxybenzophenones and some hydroxybenzotriazoles used as photostabilizers of polymers [9].

3.8. Photoreactivity of CT states towards hydrogen abstraction

The unreactivity of the triplet CT state in photoreduction reactions is confirmed. The triplet yield is still around 0.1, but the reaction quantum yield is lower than 10^{-4}, very much lower than that of a $\pi \to \pi^*$ triplet state such as that of 4-phenyl-BP [10]. The explanation of the solvent effect on the photoreactivity of PAB, which has been a feature of many textbooks, therefore stands, but it must be added that the quenching of CT states by proton transfer in protic solvents must also be considered.

4. Conclusions

The explanation for the solvent dependence of the photoreduction of PAB, which is found in many textbooks [11],

is fortunately not mistaken; it results from the switching of n–π^* and CT states in both the singlet and triplet manifolds, as the CT state energies are lowered by solvation. The CT triplet state is indeed unreactive, when it is formed in a polar, non-protic solvent such as DMF.

In protic solvents (alcohols), the triplet yield is also very low, presumably because of the quenching of the singlet excited CT state through proton transfer.

Thus the switching of n–π^* and CT states through solvation controls the triplet yield as well as the intrinsic photochemical reactivity towards hydrogen abstraction. Only the CT-type singlet state is quenched by protonation, owing to the large negative charge concentrated on the carbonyl group; in n–π^* states, the carbonyl oxygen atom is electron deficient and no quenching by protonation can take place.

Acknowledgements

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