Studies on p-nitroacetophenone triplet state

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Abstract

p-Nitroacetophenone (PNAP) triplet state properties were investigated using laser flash photolysis and phosphorescence techniques. Acetonitrile solutions of PNAP produced short-lived (approximately 3 μs) triplets on excitation at 266 nm. PNAP produced phosphorescence on excitation at 278 nm with a decay time of 15 ms. The absorption and fluorescence properties of PNAP were also investigated.

1. Introduction

p-Nitroacetophenone (PNAP) is a well-known radiosensitizer [1] belonging to the family of nitroaromatic anoxic radiosensitizers. Some of these molecules have also been shown to produce photocytotoxic properties [2,3]. PNAP has been shown to produce photodynamic reactions [4,5] on UVA illumination which are significant, especially from the photodynamic therapy (PDT) point of view (a relatively new technique for the treatment of tumours) [6]. PDT, in combination with hypoxic sensitizers (oxygen mimics), has been shown to produce significant tumour response in Dunning R3327-AT rat prostate tumour systems [7]. The phototoxic and photodynamic properties of these molecules have been attributed to the reactions of their short-lived and very reactive triplet states [8–10]. Electron abstraction by the excited triplet states of nitroaromatic sensitizers from suitable donors, such as DNA bases, has been proposed as an alternative mechanism to the donation of electrons by excited state bases to ground state sensitizers in radiation therapy [10,11]. Triplet ketones have been shown to produce cyclobutane dimers and chain breaks in DNA on illumination [12].

In this paper, PNAP triplet state properties have been investigated using laser flash photolysis and phosphorescence studies. The lifetime of the triplet state has been measured at both room temperature and 77 K. The triplet–triplet absorption spectrum and phosphorescence spectrum of PNAP have been recorded. The fluorescence properties of PNAP have been studied. The absorption properties of PNAP in various solvents, e.g. water, acetonitrile and ethanol, have been investigated.

2. Materials and methods

PNAP was obtained from Aldrich and purified further by repeated crystallization using benzene as solvent. The solvents used in the experiments were of spectral grade. Triple distilled water was used for sample preparation.

2.1. Laser flash photolysis studies

Acetonitrile solutions of PNAP (10^{-4} M) were irradiated by Q-switched Nd:YAG laser (laser energy, approximately 10 mJ) (Spectra Physics) at 266 nm (fourth harmonic). The digitized signal displayed on the oscilloscope (Iwatsu-8123) for the transient species generated was fed into a PC through a GPIB interface and analysed. Solutions were thoroughly deoxygenated by flushing with Ar for 40 min before laser flash photolysis studies.

2.2. Phosphorescence studies

Ethanol (absolute alcohol) solutions of PNAP (10^{-5} M) were excited at 278 nm and the phosphorescence properties were monitored by a Shimazdu F4010 fluorescence spectrophotometer. The phosphorescence lifetime was obtained by measuring the time taken for the radiation intensity to decay to $1/e$ of its original value.

The fluorescence properties of PNAP (5×10^{-6} M) in acetonitrile were studied using a Shimadzu F4010 fluorescence spectrophotometer. The quantum yield (Φ_F) was calculated by measuring the area under the curve using tyrosine as standard.

The absorption properties of PNAP, in water (dielectric constant $(\epsilon) = 80$), acetonitrile $(\epsilon = 37.5)$ and ethanol $(\epsilon = 26)$ were monitored using Hitachi U2000 UV–Vis spectrophotometer.

3. Results and discussion

Acetonitrile solutions of PNAP (10^{-5} M) produced an absorption spectrum in the UV region with a maximum absorbance at 263 nm as shown in Fig. 1. A similar spectrum was observed for aqueous and alcohol solutions of PNAP with a minor shift in the absorption maximum: to 258 nm for alcohol solutions and 268 nm for aqueous solutions. The molar extinction coefficient (ϵ) was 30 000 for aqueous solutions, and similar values were observed for acetonitrile and alcohol solutions of PNAP. The observed red shift of the absorption maximum of PNAP with an increase in the solvent polarity indicates that the ground state absorption of PNAP is a π,π^* transition [13].

Laser flash photolysis using 266 nm excitation of an acetonitrile solution of PNAP (10^{-4} M) produced a transient spectrum with a maximum absorbance at 340 nm as shown in Fig. 2. The decay constant of the observed transient was approximately 3.7×10^5 s^{-1} and the lifetime of the transient was of the order of 3 ± 0.2 μs. A typical oscilloscope trace of the transient is shown in Fig. 3. The transient was promptly quenched on exposure to environmental oxygen. The very short lifetime of the transient and the quenching characteristics by oxygen could indicate that the observed species is the triplet state of PNAP. Laser flash photolysis of aqueous solutions of PNAP (10^{-5} M) produced a transient at 360 nm with a long lifetime (of the order of milliseconds) which was not influenced by the oxygen concentration; the characteristics of this species indicate that it is PNAP$^{\bullet-}$ as reported earlier [14].

To confirm the formation of the triplet, phosphorescence studies of PNAP, in ethanol glass, were carried out. PNAP (10^{-5} M) in ethanol glass at 77 K produced a phosphorescence spectrum with a maximum emission at 440 nm, on excitation at 280 nm, as shown in Fig. 4. The phosphorescence lifetime was observed to be 15 ± 2 ms. A typical phosphorescence decay curve is shown in Fig. 5. Acetonitrile solutions of PNAP (5×10^{-6} M) produced a very weak fluorescence spectrum with a maximum emission around 320 nm. This can be explained as a result of the high intersystem crossing rate as usually observed for keto compounds. The quantum yield (Φ_F) of this state was observed to be approximately 5×10^{-4} as measured using the area under the curve (data not given).

The very short lifetime of the triplet, observed by both laser flash photolysis and phosphorescence, suggests that it may be the n,π^* state of the PNAP triplet. Usually n,π^* states of simple nitroaromatic triplets are very short lived and, similarly, the PNAP triplet appears to be reactive [8,11]. The relatively weak triplet–triplet absorption and phosphores-
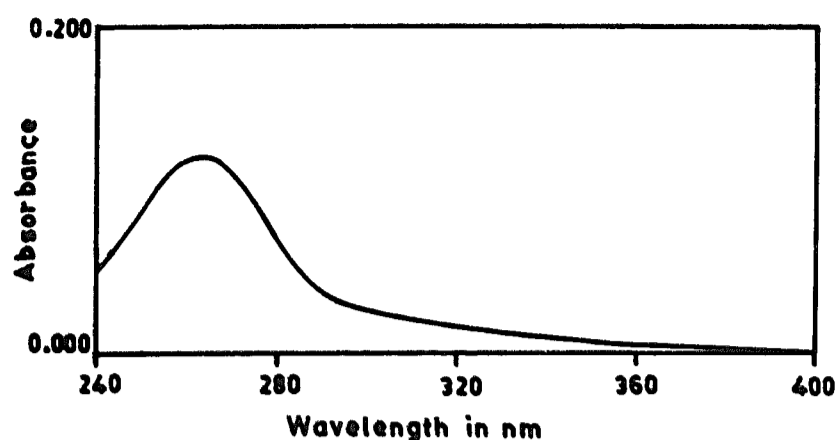

Fig. 1. Typical absorption spectrum of PNAP (5×10^{-6} M) in acetonitrile solution.
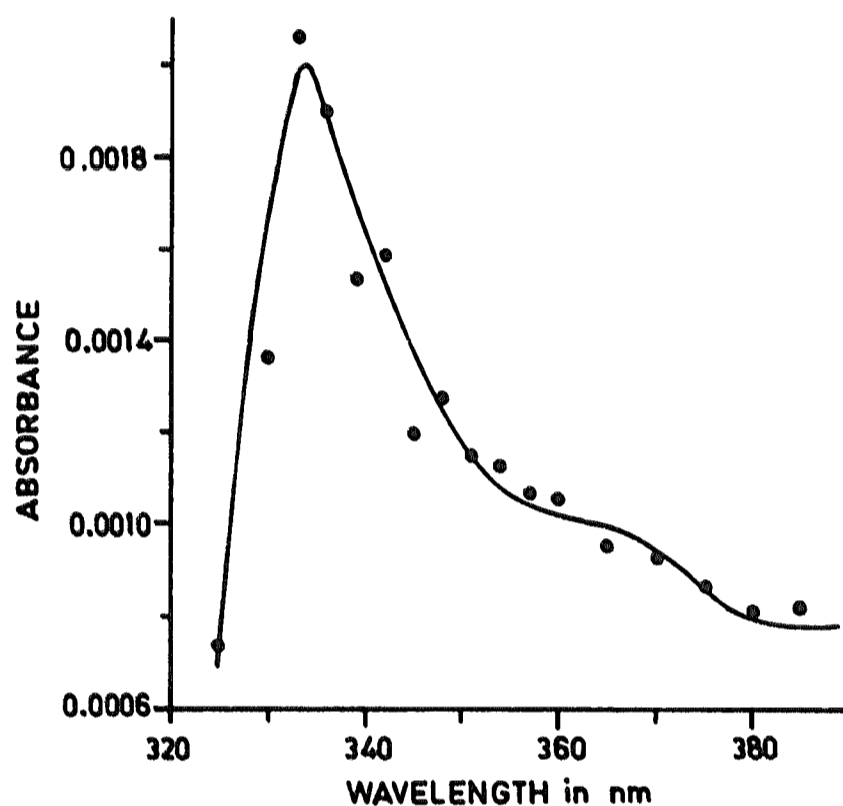

Fig. 2. Transient absorption spectrum recorded on laser flash photolysis at 266 nm of PNAP (10^{-4} M) in acetonitrile solution.
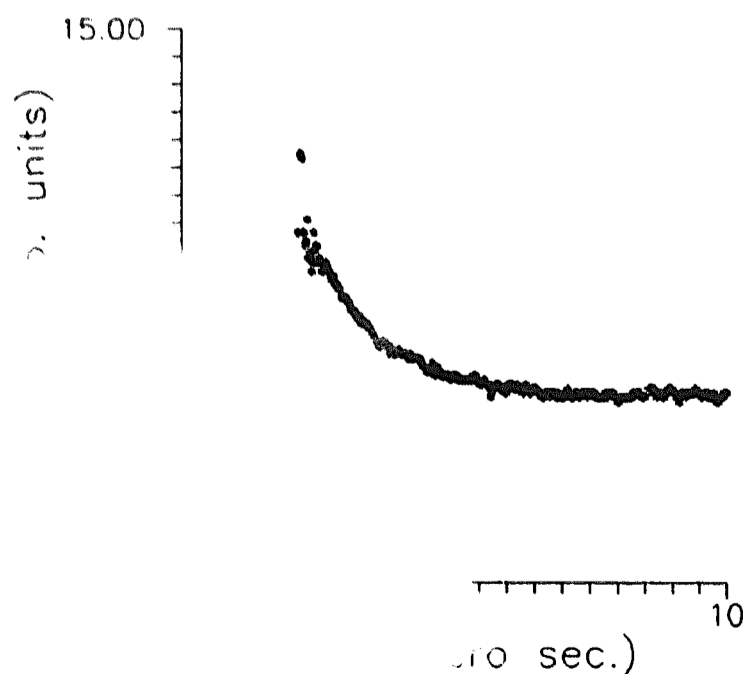

Fig. 3. K.....   ....330 nm in the laser flash photolysis of PNAP (10   ....olution.
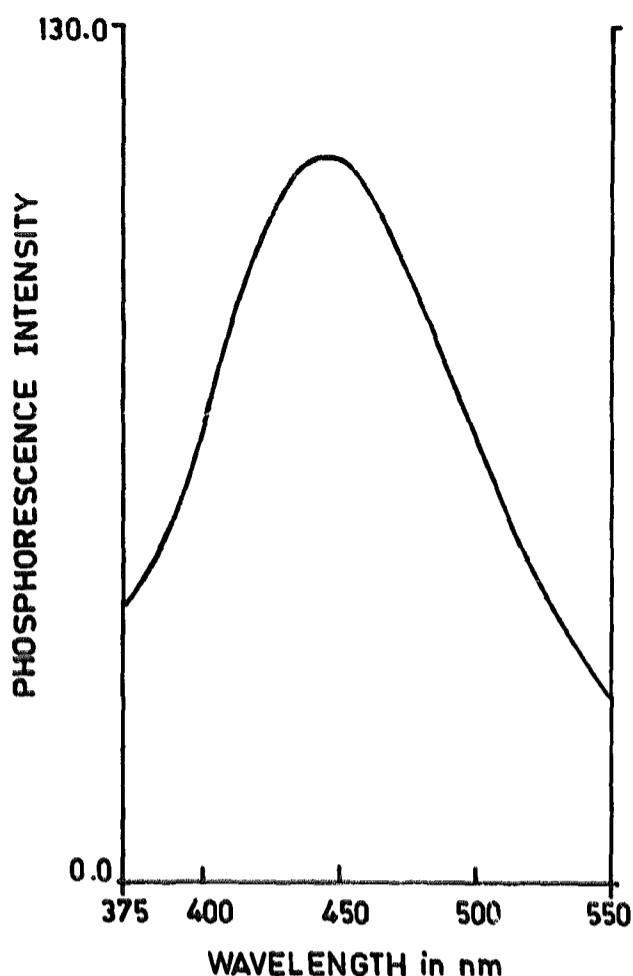
Fig. 4. Phosphorescence spectrum of PNAP (10^{-5} M) in ethanol glass at 77 K.
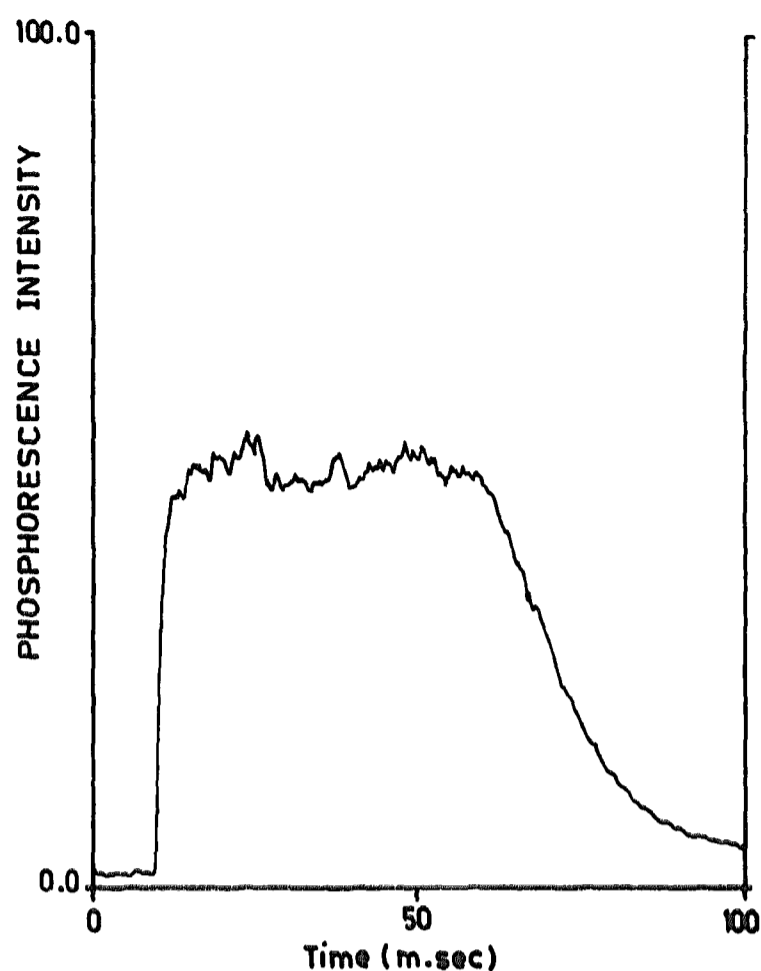

Fig. 5. Typical phosphorescence decay curve of PNAP (10^{-5} M) recorded at 440 nm, on excitation at 280 nm, in ethanol glass at 77 K.

cence spectra further corroborate this. Moreover, from solvent perturbation studies, it can be concluded that the ground state absorption of PNAP is probably due to $^1\pi,\pi^*$ and the triplet state produced by rapid intersystem crossing can be assigned as $^3n,\pi^*$ because the transition between $^1(\pi,\pi^*)$ and $^3(n,\pi^*)$ occurs readily [15].

Acknowledgements

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