DIFFUSE REFLECTANCE LASER FLASH PHOTOLYSIS STUDY OF THE PHOTOCHEMISTRY OF β-PHENYLPROPIOPHENONES ADSORBED ON MICROCRYSTALLINE CELLULOSE

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Time resolved triplet absorption and emission spectra of β-phenylpropiophenone (Ia) and its derivatives (Ib = 4-OMe, Ic = 4-Me, and Id = 4-CN) adsorbed on microcrystalline cellulose were obtained using the diffuse reflectance laser flash photolysis (DRLFP) technique. The decays related to triplet-triplet absorption spectra were non-exponential, indicating a non-homogeneous distribution of adsorption sites and different conformational restrictions. Triplet decay of Ia-b and in a less extension of Ic resulted in the formation of a long lived species which we assigned to the corresponding ketyl radicals. Dispersive kinetics analysis led to an average rate constant for phosphorescence decay of Ia-d ranging from $\bar{k}$ = (1.9 ± 0.4) x 10^6 s^{-1} (Ia) to (0.3 ± 0.1) x 10^6 s^{-1} (Id) and a width of distribution ranging from γ = 2.9 (Ia) to 2.3 (Id).

Keywords: ketones; cellulose; diffuse reflectance laser flash photolysis.

INTRODUCTION

β-Phenylpropiophenone (**Ia**; R = H) and its derivatives containing substituents in the β-phenyl ring (**Ib-i**) have frequently been used to probe cavity dimensions and mobility in organized systems[1-6]. In homogeneous solution the excited triplet state of **Ia-i** have a very short lifetime (e.g. 1 ns, in benzene, for **Ia**) due to an extremely efficient intramolecular quenching process, involving the eletrophilic carbonyl oxygen and the β-phenyl ring[7-10]. On the other hand, inclusion of **Ia-i** in the cavity of either silicalite[1,2,4,6] or cyclodextrins[3,5] results in a severe restriction to molecular motion, preventing their excited triplet state to reach the necessary conformation leading to deactivation. As a consequence, triplet lifetime for **Ia-i** is dramatically enhanced by *ca.* 5 orders of magnitude, compared to the value obtained in homogeneous solution.
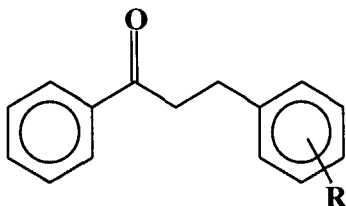
Ia; R = H
Ib; R = 4-OMe
Ic; R = 4-Me
Id; R = 3-Me
Ie; R = 3-Me

If; R = 2-Me
Ig; R = 2,4,6-triMe
Ih; R = 4-OH
Ii; R = 4-Cl

In the last few years we concentrated most of our efforts on photophysical and photochemical studies of several probes adsorbed on an almost unexplored host, microcrystalline cellulose. From these studies a large amount of information concerning triplet-triplet energy transfer[11], fluorescence[12-15] and

phosphorescence[6,16] spectroscopy, and electron[17-19] and hydrogen[20] transfer was obtained. Adsorption of probes onto submicroscopic pores of microcrystalline cellulose can be achieved when a solution containing the probe, dissolved in a hydroxylic solvent, is put in close contact with the cellulose. As a consequence, the strong hydrogen bonds between cellulose molecules are replaced by new solvent-cellulose interactions. This allows the probe to penetrate into spaces between cellulose chains, created by the swelling process. After that solvent removal leads to a breakdown of solvent-cellulose bonds, thus regenerating cellulose-to-cellulose interactions, this time leaving the probe entrapped inside the natural polymer molecules. Consequently, a reasonable decrease of the molecular mobility of the guest species is expected.

In this communication we show results on time-resolved absorption and emission studies on the photochemistry of the ketones **Ia-d**, adsorbed on microcrystalline cellulose, using the diffuse reflectance laser flash photolysis technique, which is the most convenient technique to study transient absorption and emission in non transparent, light scattering samples[21].

EXPERIMENTAL PART

β-Phenylpropiophenones were synthesized as previously described[10].

Microcrystalline cellulose Whatman, 50 μm average particle size, was dried in a vacuum oven at 70°C for 24 h before use. This species is produced by acidic hydrolysis (2.5 N HCl at 105°C for 15 min) of mechanically disintegrated cellulose, resulting in a highly crystalline material. It shows rod-like or lamelar shape, with specific internal area varying from 10 to 200 m^2/g[22,23].

Samples were prepared using a ketone : cellulose ratio of 10% wt/wt. The ketones were dissolved in a certain amount of methanol and the resulting solution was added to microcrystalline cellulose, suspended in the same solvent. Removal of methanol was done under vacuum, at low temperature, until sample dryness.

Laser flash photolysis experiments used the pulses (266 nm, 8 ns/pulse, 20 mJ/pulse) of a Spectra Physics Quanta Ray GCR-3 Nd:Yag laser for excitation. The signals from a Hamamatsu R298 photomultiplier were captured by a 2430A Tektronix digital oscilloscope interfaced to a PDP 11/73 computer. The monitoring source was a pulsed 250 W xenon lamp from Applied Photophysics. Data were recorded in a 100 μs full scale domain, at 20 ± 1°C. The same results were obtained in either degassed or aerated samples.

Diffuse reflectance laser flash photolysis (DRLFP) data are reported as percentage of absorption by the transient, expressed as $100\Delta J/J_o = (1 - J_t/J_o)100$, where J_o and J_t are diffuse reflected light from sample before exposure to the exciting laser pulse and at time t after excitation, respectively.

RESULTS AND DISCUSSION

Laser excitation of β-phenylpropiophenone (**Ia**) adsorbed on microcrystalline cellulose, at 266 nm, leads to the formation of a readily detectable transient which shows a maximum around 400 nm (Fig. 1). It is well known that triplet-triplet absorption for alkyl aryl ketones is centered at 340 nm[24], whereas their corresponding ketyl radicals show absorption around 400 nm[25]. Therefore, we tentatively assigne this transient as a mixture of the triplet state of **Ia** and the ketyl radical derived from it. The absorption for the complex under study is dominated by the considerably high amount of radical formed in this case. This is in accordance with early reports where high yields for ketyl radical formation from benzophenone included in cyclodextrins[26] or adsorbed on microcrystalline cellulose[16] were mentioned.
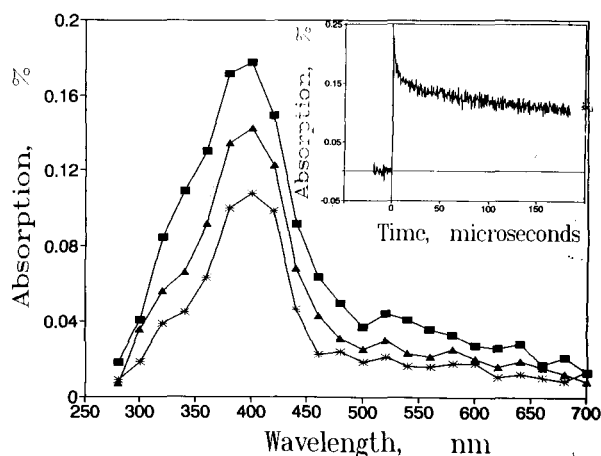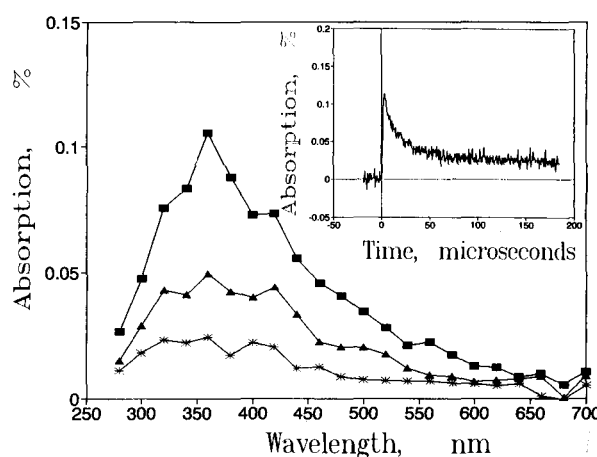

Figure 1. Time resolved absorption spectra obtained on 266 nm excitation of β-phenylpropiophenone (Ia) adsorbed on microcrystalline cellulose recorded at 2.0 μs (curve 1), 20 μs (curve 2) and 160 μs (curve 3) after laser pulse. Insert: decay at 400 nm for the transient generated as above.

The decay associated to this absorption is complex. One can observe a short lived decay superimposed to a slow decay, the later accounting for close to 60% of the absorption (Fig. 1, insert). For the short lived species, it was not possible to fit its decay using a simple monoexponential due to the fact that **Ia** is adsorbed onto different submicroscopic pores of microcrystalline cellulose. However, by using a biexponential we could obtain lifetimes of 1.5 ± 0.8 and 20 ± 0.3 μs. These values should only be viewed as an order of magnitude for the lifetimes associated to the various cellulosidic sites where different β-phenylpropiophenone conformations are located. The decay for the long lived species, measured after a 50 μs delay, was reasonably fitted by a first order kinetics, from

which we obtained a lifetime of 655 ± 48 ms. Similar spectroscopic and kinetic behavior were observed for **Ib**, R = 4-OMe.

Unlike **Ia-b**, **Ic** (R = 4-Me) and **Id** (R = 4-CN) show a quite different transient absorption spectrum. In these two cases a maximum around 360 nm was recorded (Fig. 2). Concomitantly, we could observe a dramatic decrease in the $\Delta J/J_o$ value for the long lived species formed after **Ic** excitation. For **Id**, the long lived species was pratically absent (Fig. 2, insert). These results led us to conclude that, in these two cases, the ketone is located in such an environment that prevents its triplet state to efficiently abstract hydrogen from the cellulose. Previous results on the reactivity of benzophenone in microcrystalline cellulose[16] show that diphenyl ketyl radical formation is greatly reduced if the ketone is adsorbed on the surface of cellulose and not entrapped in this host molecule. Thus, the low yield for ketyl radical formation from **Ic** (or its absence for **Id**) can be possibly due to the localization of these two probes on the surface of cellulose. However, at this point it is not clear the reasons for the difference in behavior between **Ia-b** and **Ic-d**, since neither steric nor electronic effects can account for it.

Figure 2. Time resolved absorption spectra obtained on 266 nm excitation of β-(4-cyanophenyl)propiophenone (Id) adsorbed on microcrystalline cellulose recorded at 2.0 μs (curve 1), 20 μs (curve 2) and 160 μs (curve 3) after laser pulse. Insert: decay at 360 nm for the transient generated as above.

Time-resolved phosphorescence spectra for **Ia-d** adsorbed on microcrystalline cellulose were recorded in the 320-600 nm region. In all cases the spectrum was structureless and showed a maximum at 420 nm. This is in fully accord with previous report on steady-state phosphorescence studies for these same ketones in organized systems, namely silicalite[2] and cyclodextrins[3]. Phosphorescence lifetimes obtained from these emissions using a biexponential fit are much the same as the ones recorded right after the laser pulse on absorption studies, thus confirming the ketone triplet state nature of the short lived species, as reported above. Once more, it is necessary to emphasize that values obtained by a biexponential fit give only the order of magnitude for triplet lifetimes. To overcome this problem we used dispersive kinetics[27] to extract some more relevant parameters from these decays. This method is adequate to rationalize these kind of kinetic data, since it considers a monomolecular decay, with a gaussian distribution of the logarithm of rate constants at various adsorption sites, due to the non-homogeneity of the adsorbent surface. Applying the dispersive kinetics analysis to phosphorescence decays of **Ia-d** we obtained average values ranging from $\bar{k} = (1.9 \pm 0.4) \times 10^6$ s⁻¹ (**Ia**) to $(0.3 \pm 0.1) \times 10^6$ s⁻¹ (**Id**). These values led us to conclude that the contribution of the long lived component in

the overall decay is very low. The calculated width of distribution vary from $\gamma = 2.9$ (**Ia**) to 2.3 (**Id**), in accordance with a previous reported value of 2.2 for microcrystalline cellulose, probed by benzophenone and some quinones in the presence of triphenylamine[18].

A summary of the absorption and emission data for β-phenylpropiophenones (**Ia-d**) adsorbed on microcrystalline cellulose presented in this communication is shown in Table 1.

Table 1. Summary of absorption and emission data for b-phenyl-propiophenones (**Ia-d**) adsorbed on microcrystalline cellulose.

	Ia	Ib	Ic	Id
$\lambda_{max(abs)}$, nm	400	400	360	360
$\lambda_{max(em)}$, nm	420	420	420	420
$\tau_{radical}$, μs	655 ± 48	542 ± 66	583 ± 139	—
$\tau_{1(abs)}$, μs[a]	1.5 ± 0.8	3.6 ± 1.2	2.3 ± 1.3	3.2 ± 1.3
$\tau_{2(abs)}$, μs[a]	20.0 ± 0.3	20.9 ± 3.5	20.9 ± 4.2	18.2 ± 1.2
$\tau_{1(em)}$, μs[b]	2.0 ± 0.1	1.4 ± 0.1	5.5 ± 0.4	1.7 ± 0.1
$\tau_{2(em)}$, μs[b]	16.5 ± 0.7	13.9 ± 1.2	31.7 ± 2.1	19.6 ± 0.9
$\bar{k}$ x 10^{-6}, s^{-1} [c]	1.9 ± 0.4	1.2 ± 0.4	0.9 ± 0.4	0.3 ± 0.1
γ [c]	2.9 ± 0.1	2.4 ± 0.2	2.5 ± 0.3	2.3 ± 0.2

a - triplet lifetime from absorption experiments
b - triplet lifetime from emission experiments
c - from dispersive kinetics analysis[27]

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