ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 109 (1997) 293–298

Journal of PHOTOCHEMISTRY AND PHOTOBIOLOGY A:CHEMISTRY

# Application of diffuse reflectance laser-flash photolysis to the study of aromatic probes in $\beta$-cyclodextrin solid complexes

Mónica Barra *, Kazim A. Agha [1]

*Department of Chemistry, University of Waterloo, Waterloo, Ont. N2L 3G1, Canada*

Received 20 January 1997; revised 17 March 1997; accepted 14 April 1997

## Abstract

Time-resolved diffuse reflectance laser-flash photolysis techniques were employed to study the photochemistry of benzil, naphthalene, and pyrene within $\beta$-cyclodextrin solid complexes. The photochemistry of benzil and naphthalene is dominated by their triplet state. In the case of pyrene, the formation of radical cations and radical anions is observed, in addition to the signals due to the triplet state. In all three cases triplet excited states exhibit non-exponential (multi-component) kinetics. Analysis of triplet decays by means of lifetime distributions shows that quenching by oxygen is significantly restricted within $\beta$-cyclodextrin solid complexes. This result is attributed to the protection offered by the cyclodextrin cavity, which limits the space available for diffusion and contact of reactants. © 1997 Elsevier Science S.A.

*Keywords:* Laser-flash photolysis; Aromatic probes

## 1. Introduction

The photochemical and photophysical properties of organic substrates can be significantly altered upon inclusion by host molecules in solution as well as in the solid state. Cyclodextrins (CDs), doughnut-shaped cyclic oligosaccharides of six to eight $\alpha$-D-glucose units, have been extensively studied during the past decades owing to their ability to form inclusion complexes (compounds) and, consequently, their ability to control the physical and chemical properties of included substrates [1]. While there is a large volume of data available on photophysical and photochemical properties of organic substrates complexed with cyclodextrins in solution, little is known about the effects of complexation in the solid state [2](a).

Time-resolved diffuse reflectance laser-flash photolysis is a relatively new technique which has been successfully applied to the detection of excited states at interfaces, and in various opaque and crystalline systems [3]. Application of spectroscopic techniques of this type should be of value in understanding the effects of solid state inclusion on photoinduced processes. In this context, time-resolved diffuse reflectance laser-flash photolysis techniques have recently been applied to the study of the photobehavior of aromatic ketones such as xanthone and benzophenone within CD solid complexes [4,5]. Both ketones are photoreduced upon hydrogen abstraction from CDs. In addition, the most probable benzophenone triplet lifetime is found to decrease as the size of the CD cavity decreases, whereas the opposite is observed with xanthone [5]. These differences were interpreted in terms of changes in triplet reactivity and of restrictions on the mobility of included substrates.

In order to characterize further CDs as solid hosts, time-resolved diffuse reflectance laser-flash photolysis techniques were applied to the study of the photobehavior of aromatic probes such as benzil, naphthalene, and pyrene included in $\beta$-CD (i.e. seven glucose units) solid complexes. The effect of oxygen on transient kinetics was also analyzed by means of lifetime distributions.

## 2. Experimental details

$\beta$-Cyclodextrin (Aldrich) and naphthalene (scintillation grade, Aldrich) were used as received. Pyrene (BDH) and benzil (Aldrich) were recrystallized twice before use. Dimethylsulfoxide (Omnisolv) was used as received.

Cyclodextrin solid complexes were prepared by precipitation from saturated CD aqueous solutions layered underneath concentrated solutions of the corresponding guest compounds in diethyl ether, as previously reported [4]. Host-to-guest ratios were determined by means of UV–visible

---

* Corresponding author.

[1] RISE summer student, 1996.

*PII* S1010-6030(97)00149-4

absorption spectroscopy using dimethylsulfoxide solutions, as previously described [4]. Wavelengths for quantification (and corresponding molar extinction coefficients) were as follows: benzil, 380 nm (79.5 $M^{-1}$ $cm^{-1}$); naphthalene, 278 nm ($6.47 \times 10^3$ $M^{-1}$ $cm^{-1}$); pyrene, 339 nm ($4.33 \times 10^4$ $M^{-1}$ $cm^{-1}$).

Experiments to determine the effect of oxygen on triplet decays were carried out by using two sets of inclusion complexes. One set of complexes was prepared in a glove box and, thus, kept under oxygen-free nitrogen at all times. The other set of complexes was prepared under air equilibrated conditions, and then kept under a stream of pure oxygen or oxygen-free nitrogen for 30 min.

UV–visible absorption spectra were recorded on a Varian Cary 1 Bio UV–visible spectrophotometer. Fluorescence spectra were recorded using a Perkin Elmer MPF-2A spectrofluorimeter.

The time-resolved diffuse reflectance laser-flash photolysis system employed was built based on the design of a similar system [6]. The excitation source is a Q-switched Nd/YAG laser (Continuum, Surelite I-10) operated at 355 nm (4–6 ns pulses, $<50$ mJ $pulse^{-1}$). Excitation doses are typically attenuated to less than 20 mJ $pulse^{-1}$ by using a neutral wedge. The laser beam incident upon the sample is also attenuated with a diverging lens that provides an even irradiation of the front face of the cell. The analyzing beam consists of a pulsed 75 W xenon lamp (Power Arc Compact Arc Lamp Housing and power supply model LPS 220, both from Photon Technology International). The diffusely reflected analyzing beam is collected and focused on the entrance slit (typically 1.5 mm) of a CVI Digikrom 120 monochromator. Special care was taken to minimize signals due to all specular reflections. A Hamamatsu R-446 photomultiplier tube in a six-dynode stage housing is attached to the exit slit (typically 1.5 mm) of the monochromator. A home-built computer controlled power supply sets the high voltage for the photomultiplier tube. The signal from the photomultiplier tube is connected via a 93 Ω cable (with two 93 Ω terminators) to a high pass filter which allows to offset the voltage corresponding to the light intensity before the laser pulse. The signal then goes to a Tektronic TDS 620A digitizer, which is connected via a GPIB interface (National Instruments GPIB NI-488.2 board) to a computer (Power Mac 7100/80). A timing and digital I/O interface board (National Instruments NB-TIO-10 board) is used to generate TTL pulses to open and close shutters, and to control the timing for the laser and lamp pulser. The laser system is controlled by a Power Mac 7100/80 computer operating with LabView 3.1.1 software from National Instruments. Data are reported as $\Delta J/J_0 = (J_0 - J_t)/J_0$, where $J_0$ refers to the initial reflected light from the sample (i.e. before laser excitation) and $J_t$ refers to the reflected light at time $t$ after laser excitation. Transient traces can be corrected for luminescence by subtracting a laser-only shot (i.e. monitoring beam shutter closed) from the initial signal trace. On long time scales a baseline correction is done by subtracting a monitoring beam-only shot (i.e. laser shutter closed) from the initial trace to correct for instability in the lamp pulse. Signal averaging is routinely performed to increase the signal-to-noise ratio. Time-dependent transient spectra are obtained using a point-by-point type of approach by recording kinetic traces at successive wavelength increments across a range. Solid samples, contained in quartz cells constructed of 3 mm × 7 mm Suprasil tubing, were shaken after every laser pulse to ensure the irradiation of fresh portions of sample by each laser pulse. All measurements were done at room temperature.

Lifetime distribution analyses were carried out by using the exponential series method software (special modified version for transient absorption) from Photon Technology International. The fitting function consisted of 100 exponential terms (with fixed, logarithmically spaced lifetimes) and variable pre-exponential factors. Lifetimes ranged from 10 ns (shortest lifetime allowed) to 200 μs (since in no case components of significant amplitude were obtained above this value). Alternatively, fittings of triplet decays to the Albery model [7] were carried out by using the general curve fitting procedure of Kaleidagraph 3.0.5 software from Synergy Software. The Albery model accounts for heterogeneous kinetics assuming a Gaussian distribution of the logarithm of the rate constant about some mean value, and has two adjustable parameters: a mean rate constant and the with of the distribution. Ref. [7] also gives a simple numerical procedure to obtain a convenient fitting function for this model.

## 3. Results and discussion

Laser irradiation of benzil/β-CD solid complex (host-to-guest mole ratio ≈ 6) leads to the transient absorption spectra shown in Fig. 1. The absorption band centered at ca. 480 nm is assigned to the triplet state of benzil. This band agrees very well with the triplet–triplet (T–T) absorption spectrum observed not only in cyclohexane or acetonitrile solutions of benzil (i.e. $\lambda_{max} = 480$ nm [8]), but also in benzil–silicalite samples (i.e. $\lambda_{max} = 470$ nm [9]). The T–T absorption in

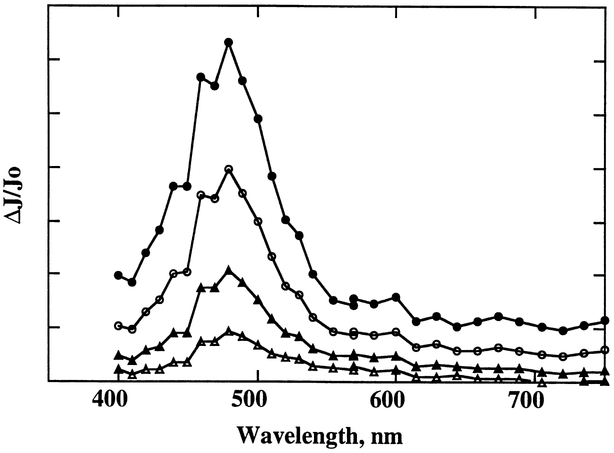

Fig. 1. Transient absorption spectra for benzil/β-cyclodextrin solid complex, obtained within 15 μs (●) and 142 μs (△) after laser pulse.

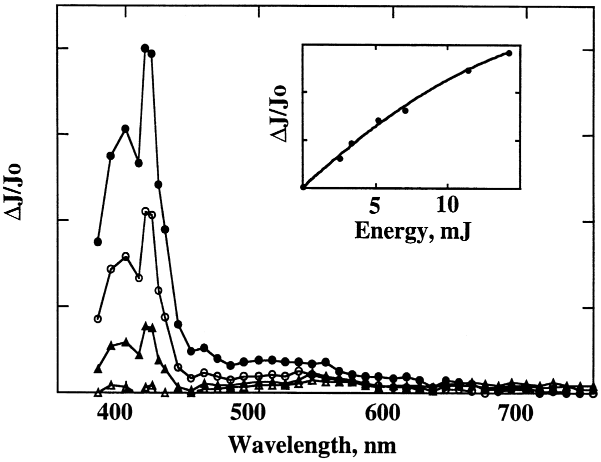

Fig. 2. Transient absorption spectra for naphthalee/$\beta$-cyclodextrin solid complex, obtained within 15 μs (●) and 141 μs (△) after laser pulse. Inset: yield of naphthalene triplet as a function of laser power.

microcrystalline benzil, on the other hand, has been shown to have $\lambda_{max}$ at 520 nm [10], a result which confirms that in the case of $\beta$-CD solid sample we are not looking at microcrystalline benzil.

In the case of naphthalene/$\beta$-CD solid complex (host-to-guest mole ratio $\approx 5$) laser excitation leads to the transient absorption spectra shown in Fig. 2. The bands at ca. 400 nm and 420 nm can be assigned to the triplet state of naphthalene by analogy to the same characteristic absorption bands observed in solution as well as in the solid state [11].

Irradiation of pyrene/$\beta$-CD solid complex (host-to-guest mole ratio $\approx 7$) leads to the transient absorption spectra shown in Fig. 3. In this case, the bands at 420 nm and 520 nm are assigned to the triplet state of pyrene [11], the band at 450 nm to pyrene radical cation [12], and that at 490 nm to pyrene radical anion [12].

No long-lived residual absorption was observed with any of the aromatic probes. Furthermore, in the case of pyrene, no time-resolved formation of radical ions could be detected up to 80 ns-per-point (shortest sampling time accessible owing to strong sample emission).

The dose dependence of triplet yields, and of pyrene radical anions and pyrene radical cations, indicates a one-photon process for all three aromatic probes, although a slight downward curvature is observed in all cases. A typical curve is shown in Fig. 2 (inset). Saturation effects of the type observed here are not uncommon in solid systems [13].

Monophotonic formation of pyrene radical ions as a result of electron transfer between pyrene molecules in the excited singlet state and those in the ground state has been recently observed in zeolites [14]. At low loading levels photoionization (Eqs. (1) and (2)) is expected to predominate, whereas at high loading levels electron transfer (Eq. (3)) becomes increasingly important.

$$\mathrm{Py}^* \rightarrow \mathrm{Py}^+ + \mathrm{e}^- \tag{1}$$

$$\mathrm{e}^- + \mathrm{Py} \rightarrow \mathrm{Py}^- \tag{2}$$

$$\mathrm{Py}^* + \mathrm{Py} \rightarrow \mathrm{Py}^+ + \mathrm{Py}^- \tag{3}$$

In the case of pyrene/$\beta$-CD solid complexes, the triplet-to-radical ion yield ratio showed no dependence on laser intensity, indicating that only one photon is required for ionization, in agreement with the dose dependence previously described. Triplet-to-radical ion yield ratios were determined as a function of host-to-guest mole ratio, and results are shown in Fig. 3 (inset). Yield ratios were calculated by simply taking the ratio of signal intensities obtained at the wavelength of maximum absorption of each of the reactive intermediates involved (i.e. triplet pyrene, 420 nm; radical cation, 450 nm; radical anion, 490 nm), immediately after laser excitation. The triplet-to-radical cation yield ratio is found to be independent of pyrene concentration. The triplet-to-anion yield ratio, however, seems to decrease gradually from a value of 0.78 (host-to-guest mole ratio 6) to a value of 0.58 (host-to-guest mole ratio 102). As a result, the radical cation-to-radical anion yield ratio tends to increase with decreasing pyrene concentration. Although details of pyrene photoionization await further investigations, the dependence of radical ion yields on pyrene concentration can be qualitatively explained assuming the occurrence of Eqs. (1)–(3). As in the case of zeolites, we expect electron transfer (Eq. (3)) to predominate at low host-to-guest mole ratios since excited pyrene molecules will not be confronted with the difficulty of finding acceptor pyrene molecules at close distance. However, keeping in mind that these complexes are far from being stoichiometric host–guest complexes, the relatively slight changes observed in triplet-to-radical ion yields, particularly at host-to-guest mole ratios $\leq 40$, seem to indicate that the number of pyrene molecules at close distance is in fact not changing dramatically among samples. Solid complexes of different host-to-guest mole ratio were prepared by limiting the amount of pyrene (relative to that of CD) initially dissolved in diethyl ether (see Section 2). In the resulting solid samples most CD cavities are empty following loss (during drying) of diethyl ether from CD–organic solvent

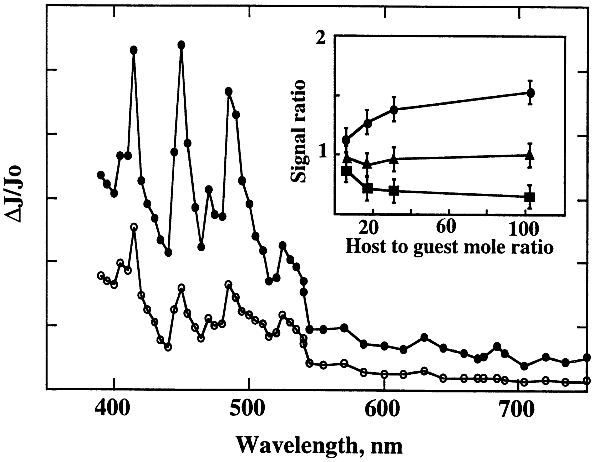

Fig. 3. Transient absorption spectra for pyrene/$\beta$-cyclodextrin solid complex, obtained at 9.6 μs (●) and 127 μs (○) after laser pulse. Inset: triplet-to-radical anion (■), triplet-to-radical cation (▲), and radical cation-to-radical anion (●) yield ratios as a function of host ($\beta$-cyclodextrin)-to-guest (pyrene) mole ratio.

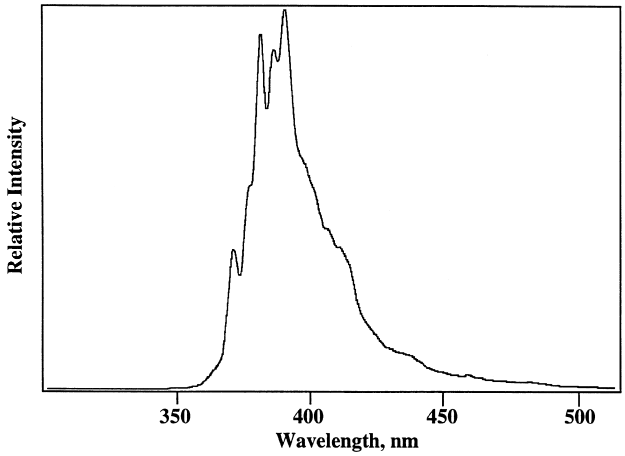

Fig. 4. Steady-state fluorescence spectrum for pyrene/$\beta$-cyclodextrin solid complex ($\lambda_{\text{excitation}}=280$ nm).

complexes (which under our experimental conditions coprecipitate). For all three aromatic probes, complexes with a channel-type structure, in which the $\beta$-CD units are piled up with the cavities aligned, are predicted [15,16]. Also, it appears that in these channel-type structures, the $\beta$-CD units prefer a dimeric head-to-head type arrangement [15]. Thus, head-to-head dimers accommodating pyrene molecules in their cavities could probably be the ones driving the precipitation. In fact, complexes of the type 1:2 and 2:2 (pyrene:$\beta$-CD) have been determined in aqueous solutions [17,18]. Thus, limiting the amount of probe initially dissolved in diethyl ether could lead to a change in the relative amounts of CD–organic solvent vs. CD–aromatic probe complexes that coprecipitate more significant than the change in the number of pyrene molecules that remain at close distance.

The absence of face-to-face intermolecular contacts between guest molecules in $\beta$-CD solid complexes has been inferred from luminescence studies. Naphthalene/$\beta$-CD solid complex fluoresces readily with $\lambda_{\max}$ at 324 nm and 335 nm (spectrum not shown), in good agreement with naphthalene emission observed in solution [19]. Pyrene, which exists essentially in excimeric orientation in crystals and, thus, is characterized by a broad emission band with $\lambda_{\max}=475$ nm (spectrum not shown), shows only monomer fluorescence when included in $\beta$-CD (Fig. 4). The vibronic fine structure of pyrene monomer emission is known to depend strongly on solvent polarity [20,21]. The solvent dependence is reflected as a marked change of the ratio between the first (0-0) and third emission bands (I/III ratio). In fluid media, the I/III ratio has been shown to vary from 0.5 (in non-polar solvents) up to 1.87 (in water) [20,21]. Consequently, pyrene has been employed as a probe of polarity in a variety of constrained media, such as micelles, vesicles (liposomes), and cyclodextrins [22]. The I/III ratio has also been used to determine the relative polarities of zeolites X and Y [23]. In the case of $\beta$-CD solid complexes, the low value of the I/III ratio (0.42) is indicative of a non-polar environment. This result emphasizes how CDs may lead to unusual photoreactions. In the case of pyrene, photoionization in non-polar solvents seems to involve biphotonic processes with either triplet [24] or singlet intermediates [25]. In $\beta$-CD solid media, albeit non-polar, only monophotonic ionization from singlet intermediates seems to take place.

With all three aromatic probes, triplet transient decay traces corresponding to (i) air-equilibrated samples, (ii) air-equilibrated samples kept under a stream of pure oxygen or oxygen-free nitrogen, and (iii) samples prepared and kept under oxygen-free nitrogen, were collected on different time scales. Typical stretched representations (i.e. reflectance change vs. log(time)) of such traces are shown in Fig. 5. Representations of this type are most convenient for systems involving transient decays covering several orders of magnitude in time scale, as usually observed in solid systems.

Not surprisingly, triplet decays within $\beta$-CD solid complexes exhibit non-exponential kinetics. The study of chemical kinetics in heterogeneous media has received considerable attention during the past decades, and several models and methods of analysis have been reported in the literature [2]b[7,26]. While a comprehensive study of such models when applied to triplet decays within $\beta$-CD solid complexes is beyond the scope of this article, preliminary dynamic analyses were carried out in an effort to determine the effect of oxygen (or lack of it) on triplet kinetics. In many heterogeneous systems, models that involve distributions of lifetimes are considered. In this context, studies related to the

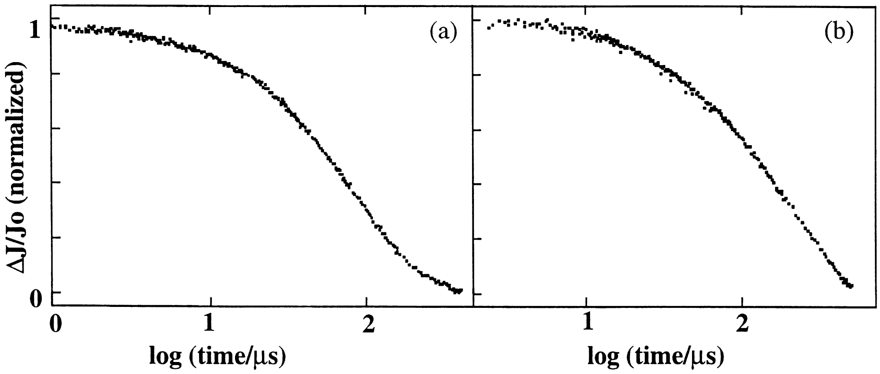

Fig. 5. Normalized triplet decay traces recorded in different time domains for benzil (a), and pyrene (b) in $\beta$-cyclodextrin solid complexes (air equilibrated samples).

application of lifetime distributions to the analysis of fluorescence decays in heterogeneous systems have been reviewed recently [2]b. Moreover, investigations on inclusion complexes of $\beta$-CD with anilinonaphthalenesulfonates in aqueous solution have shown that fluorescence decays can be described by distributed lifetimes models based on Gaussian distributions [26]b[26]c. These distributions of lifetimes are interpreted as being the result of either fluorescence probes coexisting in an ensemble of similar cyclodextrin-cavity environments [26]b, or a diversity in the conformational structure of the guests [26]c. Fits of our data to a logarithm-normal Gaussian lifetime distribution (using the Albery model [7]), however, do not provide an adequate description of triplet decay kinetics. This was indicated best by the large and systematic deviations within the residual errors (not shown), particularly at the initial part of the decay traces.

Alternatively, lifetime distribution analyses were carried out by using an exponential series method (ESM). While no attempt in ascribing physical meaning to the discrete components having significant amplitudes is made, the comparison of the number of components and contributions of the individual components among the different samples can be used as a tool to investigate oxygen effects. The results of the ESM analysis are illustrated in Fig. 6. It is clear that, with all three aromatic probes, there are at least two regions well separated. The longer-lived decay mode, dominant in all cases, accounts for at least 80% of triplet decay. The similarity between distributions in the presence and in the absence of oxygen is also quite remarkable and clear.

Table 1
Average triplet lifetimes for aromatic probes in $\beta$-cyclodextrin solid complexes

| Aromatic probe | Average lifetime $\langle \tau \rangle$ ($\mu$s) | | | |
|---|---|---|---|---|
| | Oxygen [a] | Air | Nitrogen [a] | Nitrogen [b] |
| Benzil | 63 | 56 | 64 | 68 |
| Naphthalene | 109 | 101 | 108 | 123 |
| Pyrene | 131 | 142 | 143 | 139 |

[a] Sample (air equilibrated) kept under a stream of pure oxygen or oxygen-free nitrogen for 30 min.

[b] Sample prepared and kept under oxygen-free nitrogen.

From the resulting ESM distributions average lifetimes $\langle \tau \rangle$ were calculated according to Eq. (4) [2],

$$\langle \tau \rangle = \sum_{i=1}^{N} \alpha_i \tau_i^2 / \sum_{i=1}^{N} \alpha_i \tau_i \qquad (4)$$

where $\alpha_i$ represents the contribution of an $i$th component, $\tau_i$ is its lifetime, and $N$ is the number of components of the fit. The resulting $\langle \tau \rangle$ values (Table 1) were independent of the laser intensity as well as the host-to-guest mole ratio. Interestingly, $\langle \tau \rangle$ values increase as the size of the included probe

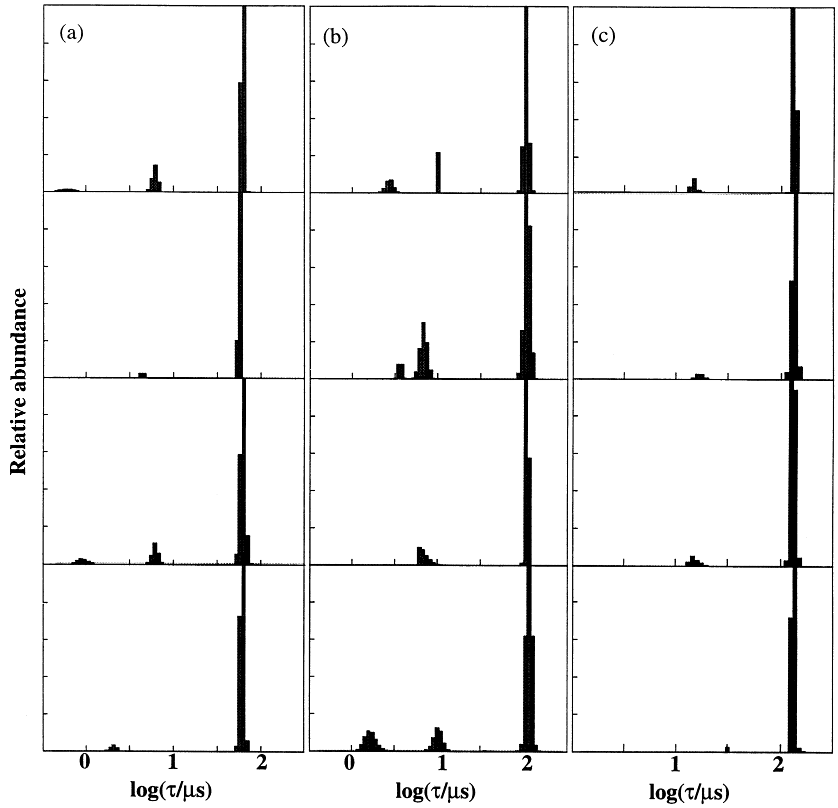

Fig. 6. Triplet lifetime distributions for (a) benzil, (b) naphthalene, and (c) pyrene. From top to bottom: (i) air equilibrated sample kept under a stream of pure oxygen for 30 min, (ii) air equilibrated sample, (iii) air equilibrated sample kept under a stream of oxygen-free nitrogen for 30 min, and (iv) sample prepared and kept under oxygen-free nitrogen.

also increases. Comparison of such data also clearly indicates that triplet quenching by oxygen is significantly restricted within $\beta$-CD solid complexes, as no significant differences outside experimental error are observed (errors are ca. ±15%). This observation is in agreement with the fact that no dependence of transient signal intensity on oxygen concentration could be detected in any case. Fig. 6 also shows that, although the number of components and the contributions of the individual components vary from sample to sample, the differences in distributions in the presence and in the absence of oxygen are not substantial.

Although a lack of oxygen effect has previously been observed in cyclodextrin solid complexes based on product distribution analysis [2]a, and indicated in the photochemical study of benzophenone included in $\beta$-CD [5], no kinetic evidence has been presented previous to this work. The lack of triplet quenching by oxygen within $\beta$-CD complexes contrasts with the dramatic effects generally observed in other supporting media such as zeolites. In the case of benzil adsorbed in Silicalite, for example, lifetimes measured under air were reduced by a factor of ca. 20 from those obtained under nitrogen [9]. Lack of oxygen effect, however, was observed when using microcrystalline benzil [10]. Differences in oxygen reactivity in solid systems have been rationalized on the basis of the ability of oxygen to diffuse into the site of reaction which, in turn, is controlled by crystal structure [27,28]. In the case of zeolites, oxygen generally can move freely and quench the excited states very effectively. In the case of our $\beta$-CD complexes, on the other hand, the space limitation would be unfavorable for diffusion and close contact of reactants. In fact, benzene has been shown to have maximum host–guest contact with the cavity of $\beta$-CD, as the volumes of the host cavity and guest are similar [29].

In conclusion, the photochemistry of benzil, naphthalene, and pyrene within $\beta$-CD solid complexes is dominated by their triplet state. In the case of pyrene, monophotonic ionization leading to the formation of radical anions and cations is also observed. Interestingly, triplet quenching by oxygen is significantly restricted within these $\beta$-CD solid complexes. This result is ascribed to the protection offered by the CD cavity, which limits the space available for diffusion and contact of reactants.

## Acknowledgements

This research was supported by the Natural Sciences and Engineering Research Council of Canada. The University of Waterloo is also gratefully acknowledged for providing start-up funds. Special thanks are due to Mr J. Szubra and Mr D. Rider for technical assistance.

## References

[1] J. Szejtli, Cyclodextrins and their Inclusion Complexes, Akadémiai Kiadó, Budapest, 1982.
[2] (a) V. Ramamurthy, in: V. Ramamurthy (ed.), Photochemistry in Organized and Constrained Media, VCH Publishers, New York, 1991, p. 303. (b) W.R. Ware, in: V. Ramamurthy (ed.), Photochemistry in Organized and Constrained Media, VCH Publishers, New York, 1991, p. 563.
[3] F. Wilkinson, G. Kelly, in: J.C. Scaiano (ed.), Handbook of Organic Photochemistry, Vol. 1, CRC Press, Boca Raton, FL, 1989, p. 293.
[4] M. Barra, C. Bohne, J.C. Scaiano, Photochem. Photobiol. 54 (1991) 1.
[5] M. Barra, J.C. Scaiano, Photochem. Photobiol. 62 (1995) 60.
[6] S. Kazanis, A. Azarani, L.J. Johnston, J. Phys. Chem. 95 (1991) 4430.
[7] W.J. Albery, P.N. Barlett, C.P. Wilde, J.R. Darwent, J. Am. Chem. Soc. 107 (1985) 1854.
[8] M.V. Encinas, J.C. Scaiano, J. Am. Chem. Soc. 101 (1979) 7740.
[9] F. Wilkinson, C.J. Willsher, H.L. Casal, L.J. Johnston, J.C. Scaiano, Can. J. Chem. 64 (1986) 539.
[10] F. Wilkinson, C.J. Willsher, Appl. Spectrosc. 38 (1984) 897.
[11] I. Carmichael, G.L. Hug, J. Phys. Chem. Ref. Data 15 (1986) 1.
[12] H. Schomburg, H. Streak, A. Weller, Chem. Phys. Lett. 22 (1973) 1.
[13] D. Oelkrug, W. Honnen, F. Wilkinson, C.J. Willsher, J. Chem. Soc., Faraday Trans. 2 83 (1987) 2081.
[14] S. Hashimoto, Chem. Phys. Lett. 252 (1996) 236.
[15] W. Saenger, J. Inclusion Phenom. 2 (1984) 445.
[16] W. Saenger, Isr. J. Chem. 25 (1985) 43.
[17] W. Xu, J.N. Demas, B.A. DeGraff, M. Whaley, J. Phys. Chem. 97 (1993) 6546, and references given therein.
[18] H.E. Edwards, J.K. Thomas, Carbohydr. Res. 65 (1978) 173.
[19] I.B. Berlman, Handbook of Fluorescence Spectra of Aromatic Molecules, Academic Press, New York, 1965, p. 104.
[20] K. Kalyanasundaram, J.K. Thomas, J. Am. Chem. Soc. 99 (1977) 2039.
[21] D.C. Dong, M.A. Winnik, Photochem. Photobiol. 35 (1982) 17.
[22] K. Kalyanasundaram, Photochemistry in Microheterogeneous Systems, Academic Press, Orlando, FL, 1986.
[23] X. Liu, K.-K. Iu, J.K. Thomas, J. Phys. Chem. 93 (1989) 4120.
[24] L.P. Gary, K. de Groot, R.C. Jarnagin, J. Chem. Phys. 49 (1968) 1577.
[25] J.L. Metzger, H. Labhart, Chem. Phys. (1975) 150.
[26] The detailed literature on heterogeneous kinetics cannot be covered in this report, only a few representative articles are listed here. (a) K.F. Scott, J. Chem. Soc., Faraday Trans. I 76 (1980) 2065. (b) F.V. Bright, G.C. Catena, J. Huang, J. Am. Chem. Soc. 112 (1990) 1343. (c) A. Nakamura, K. Saitoh, F. Toda, Chem. Phys. Lett. 187 (1991) 110.
[27] G. Alder, Isr. J. Chem. 10 (1972) 563.
[28] P. Arjunan, V. Ramamurthy, K. Venkatesan, J. Org. Chem. 49 (1984) 1765.
[29] L. Pang, M.A. Whitehead, Supramol. Chem. 1 (1992) 81.