

Study of bimolecular processes in ternary cyclodextrin complexes in the solid state by diffuse reflectance laser flash photolysis

Miquel Mir^a, Francis Wilkinson^{a,*}, David R. Worrall^a, Jose L. Bourdelande^b, Jordi Marquet^{b,*}

^aDepartment of Chemistry, Loughborough University, Loughborough, Leicestershire, LE11 3TU, U.K.

^bDepartament de Química, Universitat de Barcelona, 08193 Bellaterra, Barcelona, Spain

Accepted 24 July 1997

Abstract

The photochemistry of binary inclusion complexes of 4-nitroveratrole (NV) and *p*-dinitrobenzene (DNB) with β -cyclodextrin (β -CD) and of ternary inclusion complexes of NV or DNB and 1-phenylethylamine (PhE:V) with β -CD has been examined in the solid state by diffuse reflectance laser flash photolysis. The binary NV/ β -CD complex shows a transient absorption signal assigned to the triplet excited state of NV. The binary DNB/ β -CD complex shows a transient signal assigned to the protonated radical anion of DNB formed via hydrogen abstraction from the β -CD cavity. Laser excitation of the ternary complexes generates the corresponding radical ion pairs via photoinduced electron transfer from the amine to the nitroaromatic triplet state. Comparison with previously described conventional laser flash photolysis studies in solution shows that the investigation of solid ternary CD inclusion complexes by diffuse reflectance laser flash photolysis is valuable in the case of bimolecular photoreactions that are difficult to study in solution due to the existence of other competitive processes. © 1997 Elsevier Science S.A.

Keywords: Bimolecular processes; Diffuse reflectance laser flash photolysis; Solid state; Ternary cyclodextrin complexes

1. Introduction

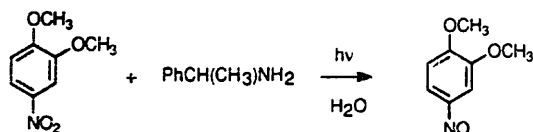
The study of photochemical processes in organized media has received increasing attention in recent years (see, for example, Refs. [1–3] and references cited therein) because of the potential of these media to alter the photophysics and photochemical reactivity of substrates relative to that observed in isotropic media (as well as other reasons [4]). The different types of organized media investigated include molecular crystals, micelles, microemulsions, Langmuir–Blodgett films, zeolites and host–guest molecular complexes. Of these, the latter, and in particular cyclodextrin (CD) inclusion complexes, are amongst the most extensively studied [1–3].

CDs are cyclic oligosaccharides of six to eight α -D-glucose units which possess internal hydrophobic cavities able to include a large variety of guest molecules in aqueous solutions [5–7]. CDs composed of six, seven and eight glucose units are termed α -CD, β -CD and γ -CD respectively. Changes in the photophysics and photochemistry of the guest molecules included in CD cavities [8–11] may be due to several effects: specific interactions between the guest and

the CDs [12]; specific photoreactions between the guest and the CDs [13,14]; sensitivity of guest photoprocesses to the polarity of the environment [14]; protection from quenching by oxygen or other quenchers [15]; constraints imposed by the cavity on the conformations of the guest molecules and on the translational and rotational motions of the photoinduced intermediates [16,17]. Such changes in properties are more pronounced in solid CD complexes [18]. In the solid state, although some progress in synthetic photochemistry has been made [18], e.g. CD complexes inducing selectivity in photochemical reactions, only a few studies [14,15,19–21] have been performed on the excited state dynamics by investigation of the photochemical transients and their kinetic behaviour, mainly using the technique of diffuse reflectance laser flash photolysis (DRIFP) developed by Wilkinson and coworkers [22–24]. These studies have been restricted to unimolecular deactivation of triplet excited states, or to photochemical hydrogen atom abstraction from the CD by the excited guest molecule within the cavity. Hitherto, no DRIFP studies have been reported on photochemical bimolecular processes between dissimilar reagents included in a solid CD phase.

The formation of inclusion complexes with CDs has been used to improve the efficiency of photoinduced electron trans-

* Corresponding authors.



Scheme 1.

fer (PET) processes [25–28] mainly by lowering the back electron transfer rate due to the constraints imposed by the cavity on the photogenerated intermediates. Previously, we reported [29] the totally selective photoreduction of certain nitrophenyl ethers by 1-phenylethylamine (PhEA) in solid β -CD ternary inclusion complexes (Scheme 1). Mechanistic studies in aqueous solution suggest [30] that a molecule of PhEA can photoreduce the nitro group of a nitrophenyl ether molecule to the nitroso group via a process initiated by PET from PhEA to the triplet excited state of the nitroaromatic compound. Therefore this photoreduction process constitutes an interesting example for the study of bimolecular processes, and in particular PET processes, in CD inclusion complexes in the solid state.

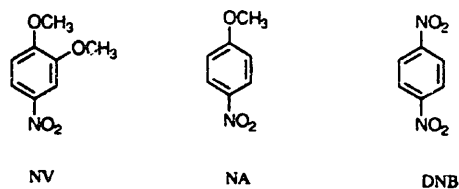
In this paper, we report a DRLFP study of the solid binary inclusion complexes of 4-nitroveratrole (NV) and *p*-dinitrobenzene (DNB) with β -CD and of their β -CD solid ternary inclusion complexes with PhEA. In the case of NV, we compare the results obtained here with those reported previously [31] with different amines in aqueous solution using conventional laser flash photolysis.

2. Experimental section

β -CD, cellulose (powder, 20 μm), silica (grade 633, 200–425 mesh, 60 Å), 4-nitroanisole (NA), NV, DNB and PhEA, supplied by Aldrich, were used as received. NA, NV and DNB have the structures shown in Scheme 2. Distilled water was used to prepare the solutions.

Solid CD complexes were prepared by dissolving a certain amount of the compound in 0.011 M β -CD aqueous solution with magnetic stirring at 70 °C for 4 h. After evaporation of water in vacuo with a rotary evaporator, the solid obtained was dried in vacuum at 40 °C for 4 h. Sample loadings are given in the text as molar ratios.

Mechanical mixtures of similar concentration to that employed for the binary solid complex DNB/ β -CD were obtained by mixing the appropriate amount of DNB with cellulose or silica. A mechanical mixture of similar concen-



Scheme 2.

tration to that employed for the ternary solid complex NV/PhEA/ β -CD was obtained by mixing the appropriate amount of NV and β -CD with a PhEA/ β -CD binary complex in an agate mortar. The binary PhEA/ β -CD complex was precipitated directly from water at room temperature after 2 h of magnetic stirring at 70 °C. These mechanical mixtures were also dried in vacuum at 40 °C for 4 h.

Time-resolved DRLFP experiments were carried out by exciting samples with frequency-tripled (354.7 nm, 10 mJ) or frequency-quadrupled (266 nm, 22 mJ) pulses from an Nd-YAG laser (HY200, Lumonics) which had a pulse width of 8 ns. A 275 W xenon lamp was used as the monitoring source, and an R928 Hamamatsu photomultiplier was used as the detector. Transient data were acquired by a Tektronix 2432A digital oscilloscope interfaced to a microcomputer. The details of this system and data treatment can be found elsewhere [24]. The parameter used to quantify the transient diffuse reflectance spectra was $\Delta J/J_0$, the fractional change in the diffuse reflectance, where J_0 is the intensity of the diffuse reflected analysing light scattered by the sample before firing of the laser pulse.

Unless otherwise indicated, all the measurements were performed at room temperature with air-equilibrated samples. Samples were shaken between laser shots to ensure that a fresh surface was exposed each time.

Ground state diffuse reflectance absorption spectra were recorded on a Phillips PU8800 UV-visible spectrophotometer equipped with an integrating sphere.

3. Results

It is known that nitroaromatics [32,33] and PhEA [34] form inclusion complexes with CDs in aqueous solution. Previous results [29,35] suggest that all the compounds employed in the present work form inclusion complexes in aqueous media and in the solid state.

3.1. Binary complexes

Irradiation at 355 nm of air-equilibrated solid binary NV/ β -CD complexes in the molar ratio 0.04 : 1.00 yields a transient with an absorption maximum at 480 nm (see Fig. 1(a) for the spectrum and Fig. 1(b) for the decay trace). This transient absorption resembles the triplet state of NV in non-hydrogen-bonding solvents [35], where the peak of the transient absorption occurs, for example, at 480 nm in acetonitrile solution.

Irradiation at 355 nm of air-equilibrated solid binary NA/ β -CD complexes in the molar ratio 0.07 : 1.00 yields no detectable transient absorption.

Irradiation at 266 nm of air-equilibrated solid binary DNB/ β -CD complexes in the molar ratio 0.03 : 1.00 yields a transient with an absorption maximum at less than 390 nm (see Fig. 2). It was not possible to record the spectra below 390 nm because the analysing light caused photodegradation of

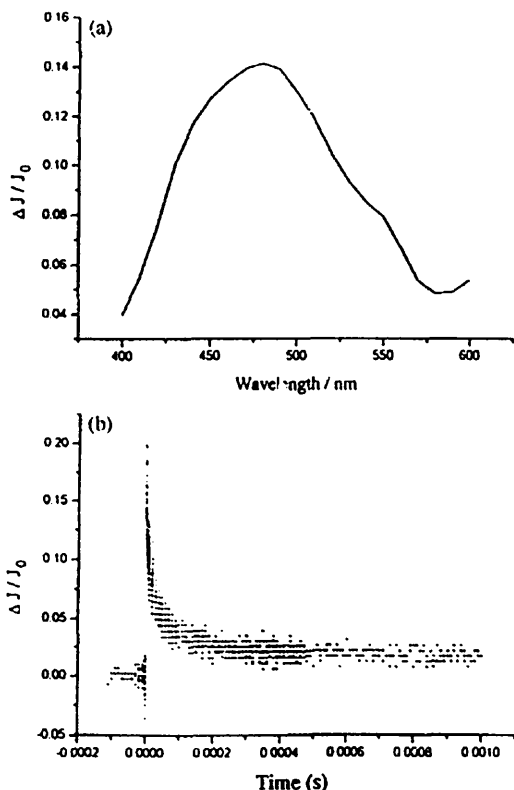


Fig. 1. (a) Transient absorption spectrum for binary NV/ β -CD solid inclusion complex obtained within 1.7 μ s after the laser pulse at 355 nm. (b) Transient decay trace monitored at 480 nm for binary NV/ β -CD solid inclusion complex.

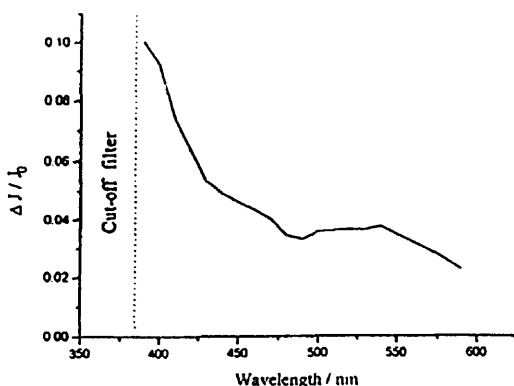


Fig. 2. Transient absorption spectrum for binary DNB/ β -CD solid inclusion complex obtained within 290 μ s after the laser pulse at 266 nm. A cut-off filter was used to prevent photodegradation of the sample and so data collection below 390 nm was not possible.

the sample. For this reason, a cut-off filter with zero transmittance below 390 nm was interposed between the arc lamp and the sample. The same transient with a lower signal intensity was obtained on photoexcitation at 355 nm.

It is known that the triplet state of *p*-nitroacetophenone can abstract hydrogen atoms from CDs within the inclusion complex on UV irradiation in aqueous solution [36]. Nitroaromatic compounds substituted with electron-withdrawing groups, such as DNB and *p*-nitroacetophenone, where the lowest lying triplet state is of n, π^* character [37–41], have a much higher tendency to abstract hydrogen atoms than nitroaromatics with electron-donating substituents, where the lowest lying triplet state is of π, π^* character [37–41]. Moreover, nitroaromatic compounds without electron-donating groups, having lowest lying triplet states of n, π^* character, show very short lifetimes, in the range of picoseconds in solution [42]. In this work, no transient was observed when the binary complex of NA with β -CD was subjected to laser excitation. NA is a nitroaromatic with more tendency than DNB to have a lowest lying triplet of π, π^* character and, therefore, with a triplet state expected to have a slightly longer lifetime [43] than that of DNB but with less tendency to abstract hydrogen atoms [37–41]. This suggests that the transient observed when DNB/ β -CD samples are subjected to DRLFPP may be due to the radical formed via hydrogen abstraction from β -CD following excitation of the nitro group.

This assignment is supported by the fact that nanosecond laser flash photolysis (excitation of DNB at 266 nm in 2-propanol) leads to a transient with a maximum around 360 nm. This transient has previously been identified as the conjugate acid of the DNB radical anion using the technique of photochemically induced dynamic nuclear polarization (photo-CIDNP) [39]. Therefore the observed λ_{max} of the transient from the solid DNB/ β -CD complex is consistent with our assignment that this absorption is due to the protonated radical anion formed through hydrogen abstraction by the triplet state of DNB.

In order to confirm this assignment of the transient observed with the DNB/ β -CD complex, DRLFPP studies of mechanical mixtures of DNB with cellulose and silica were performed, the former having a far greater capacity to act as a hydrogen atom donor [44]. With cellulose, the same transient as obtained with the β -CD complexes was observed. With silica, no transient absorption was obtained in the 390–700 nm range following DRLFPP, irrespective of whether the sample was aerated or deaerated. These results suggest that the formation of this transient is only possible if triplet DNB molecules can abstract hydrogen atoms from a suitable donor, and therefore we assign this transient to the protonated radical anion. The fact that the triplet of DNB could not be detected from a deaerated silica sample on the nanosecond timescale is presumably due to the short triplet lifetimes of nitroaromatics without electron-donating groups [42,43]. It is worth noting that a deaerated sample of a mechanical mixture of silica and NV, which contains electron-donating groups, showed a transient signal attributable to the triplet state of NV at 480 nm on photoexcitation with the laser at 355 nm.

In order to support further the assignments of these transients as the triplet state for NV and the protonated radical

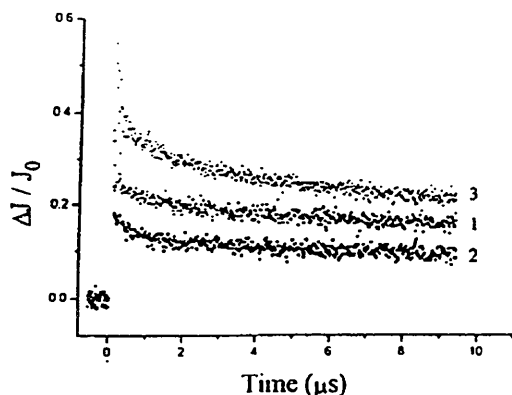


Fig. 3. Transient decay traces monitored at 460 nm for: (1) binary NV/ β -CD solid inclusion complex; (2) ternary NV/sorbic acid/ β -CD solid inclusion complex; (3) ternary NV/PhEA/ β -CD solid inclusion complex. All the samples have the same concentration of NV.

anion for DNB, quenching experiments with sorbic acid were performed. Sorbic acid is a conjugated diene which is an excellent quencher of triplet states through energy transfer [45]. It has been used [45] as a quencher for substrates with triplet energies of about 60 kcal mol⁻¹ and nitrobenzenes have similar triplet energies [42,46]. It has been reported that potassium sorbate acts as a quencher of the triplet states of nitrophenyl ethers [47,48]. Sorbic acid has also been used [49] as a quencher in the presence of CDs in aqueous solution. Moreover, it is known [50] that potassium sorbate is included in the CD cavity in aqueous solution and, presumably, its neutral analogue will have a higher tendency to be included in the less polar environment of the CD cavity. Therefore sorbic acid was used in attempts to quench triplet excited nitrobenzenes.

Excitation at 355 nm of a solid ternary complex of NV and sorbic acid with β -CD in the molar ratio 0.04 : 0.64 : 1.00 leads to the same transient as obtained with the binary complex of NV, with similar decay kinetics, but with a lower initial transient signal (Fig. 3), consistent with static quenching occurring within the duration of the laser pulse for the NV molecules in close proximity to sorbic acid molecules. This result is consistent with the assignment of the transient observed as either the triplet state of NV or a transient formed from the NV triplet state.

Excitation at 266 nm of a solid ternary complex of DNB and sorbic acid with β -CD in the molar ratio 0.03 : 0.70 : 1.00 does not lead to any transient in the 390–700 nm range; however, sorbic acid absorbs at 266 nm. Excitation at 355 nm of the same complex leads to the same transient as obtained with the binary complex of DNB with a similar transient intensity and decay. The fact that the transient was not affected by the triplet quencher is consistent with the assignment of the transient observed as the protonated radical anion of DNB, although it is interesting to note that sorbic acid does not affect the hydrogen atom abstraction reaction which suggests that this reaction is very fast indeed.

The decay trace of the binary NV/ β -CD complex transient, expressed as $\Delta I/I_0$, does not follow a simple kinetic law. It can be fitted as two monoexponentials, yielding lifetimes of 50 μ s and 1.8 ms respectively for the short- and long-lived components. The kinetic trace in Fig. 1(b) was obtained by a combination of four individual decays recorded using different timescales. Experiments with variable laser fluence do not show significant changes in the shape of the decay trace, suggesting that triplet–triplet annihilation does not contribute to the triplet decay. The same transient decay was observed when the sample was degassed prior to excitation, presumably due to the protection offered by the CD to any oxygen quenching of the triplets included in the CD in the solid state [14,15,19–21]. It should be noted that the decay of the NV triplet in the β -CD inclusion complex in the solid state is much slower than in solution, where its lifetime is reported to vary between 0.2 and 2.2 μ s depending on the solvent [31,35]. Enhanced triplet lifetimes have been observed for other substrates adsorbed on solid supports or included within solid supports; for example, the triplet lifetime of β -phenylpropiophenone is increased by five orders of magnitude in the channels of sodalite [51,52].

The decay trace at 390 nm for the binary DNB/ β -CD complex shows that the transient is very long lived (not shown).

3.2. Ternary complexes

Excitation at 355 nm of a solid ternary complex of NV and PhEA with β -CD in the molar ratio 0.04 : 0.35 : 1.00 yields a transient absorption with a maximum at 480 nm (Fig. 4) monitoring on short timescales. At longer timescales, the transient absorption shifts to give a maximum absorption at 450 nm (Fig. 4). This second transient was not observed with binary NV/ β -CD complexes. The former transient resembles the triplet state of NV observed previously in the binary NV/ β -CD complex. The absorption spectra of the triplet of NV and the radical anion of NV, which is the first intermediate

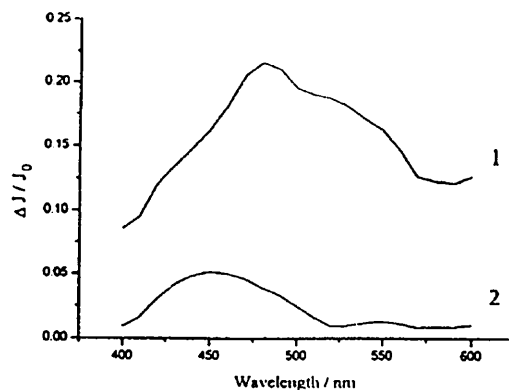


Fig. 4. Transient absorption spectra for ternary NV/PhEA/ β -CD solid inclusion complex obtained within 1.7 μ s (1) and 140 μ s (2) after the laser pulse at 355 nm.

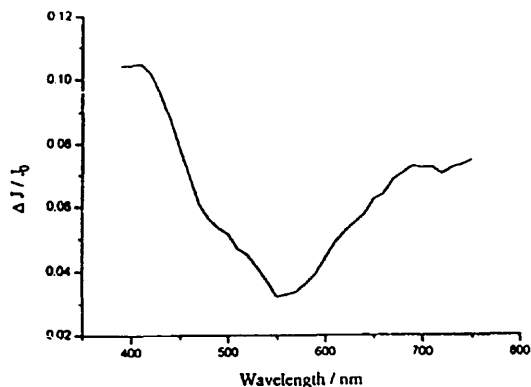


Fig. 5. Transient absorption spectrum for ternary DNB/PhEA/ β -CD solid inclusion complex obtained within 83 μ s after the laser pulse at 266 nm. A cut-off filter was used to prevent photodegradation of the sample and so data collection below 390 nm was not possible.

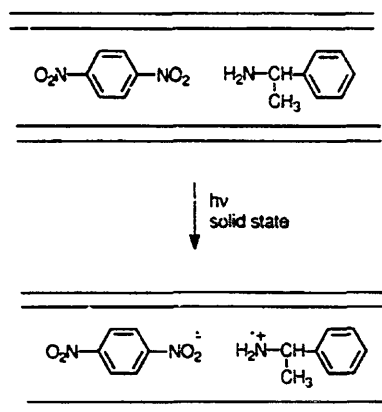
in the photoreduction mechanism, [30], have a similar shape and position in non-hydrogen-bonding solvents [53]. In order to clarify whether this transient is the NV triplet or the NV radical anion, we monitored the transient decay at 460 nm of an NV/ β -CD binary complex and an NV/PhEA/ β -CD ternary complex with equal NV loading. These transient decays are shown in Fig. 3. A higher transient absorption intensity in the ternary complex suggests that another transient has been formed, which has a higher absorption coefficient and a similar absorption spectrum to that of the NV triplet. This new transient may be the NV radical anion. The transient observed on longer timescales is more difficult to assign, and may be either a transient produced during the photoreduction process or a superposition of several transients, including the radical anion and the triplet.

A solid mechanical mixture of NV, β -CD and the PhEA/ β -CD binary complex, with similar concentrations as those employed for the ternary NV/PhEA/ β -CD complex, shows a transient assigned to the NV triplet state, but no other transient is observed at longer times.

Photoexcitation at 266 nm of the ternary sample of DNB and PhEA with β -CD in the molar ratio 0.03 : 0.52 : 1.00 leads to a transient absorption formed within the laser pulse duration. The spectrum shows two absorption maxima around 410 and above 700 nm (Fig. 5). This transient is clearly different from that observed in the binary DNB/ β -CD complex. This long-lived transient absorption is assigned to the DNB radical anion on the basis of literature data [54].

4. Discussion

It is known that CDs can act as hydrogen atom donors for triplet states of carbonyl compounds in solid complexes [14,20]. The results presented here show that β -CD can also act as a hydrogen atom donor for some nitroaromatic triplets (with low-lying triplet states of n,π^* character) [37–41] in



Scheme 3.

solid complexes. A similar conclusion was reached in aqueous solution [36].

PET from PhEA to excited NV and DNB is observed in the ternary complexes, presumably because β -CD inclusion complexes generally crystallize with a channel-like structure [55]. In such tubular structures, contact between the two reactants is possible, enabling electron transfer to occur on photoexcitation (see Scheme 3 for DNB).

No time-resolved information regarding the rate of the PET process could be obtained due to the fact that, at least in the DNB case, this process occurs within the duration of the laser pulse. In the NV case, the overlapping [53] of the triplet and radical anion absorption spectra makes it difficult to abstract information about the kinetic behaviour.

The fact that the PET process does not occur in a mechanical mixture of NV, β -CD and PhEA/ β -CD with similar concentrations as those employed for the ternary NV/PhEA/ β -CD complex suggests that the photochemical process observed in the ternary complex only occurs if preorganization of the reactants takes place during the formation of the ternary complex. The driving force for this self-organization is probably the formation of hydrogen-bond interactions between the nitro and amino groups. The existence of intermolecular hydrogen-bond interactions between nitroaromatic compounds and amines has been reported [56,57] in the literature. It has also been reported [58] that solid molecular complexes between nitroaromatic compounds and amines are formed which, on irradiation, give mixtures of several photoreduction products.

The fact that the radical anion of DNB is observed immediately following the laser pulse for the ternary DNB/PhEA/ β -CD complex means that the PET process occurs in less than 8 ns. This result further supports the existence of preorganization of the reactants in such inclusion complexes. The fact that, in such ternary complexes, the PET process can be competitive with hydrogen atom abstraction from the β -CD cavity provides further support for the formation of hydrogen-bond interactions between the nitro and amino groups,

because the formation of hydrogen bonds stabilizes the π, π^* triplet states of nitroaromatic compounds [43] and, as pointed out above, π, π^* triplet states have little tendency to abstract hydrogen atoms [37–41].

Although PET processes have been studied in solid CD complexes by time-resolved electron spin resonance (ESR) [28], as far as we know, this is the first time that the technique of DRLFP has been applied to the study of such processes.

It is interesting to note the remarkable differences in the photobehaviour observed for NV in the presence of amines in solid ternary complexes and in aqueous solution. In aqueous solution [31], in addition to the formation of photosubstitution products during NV triplet decay, an ensemble of σ complexes with broad absorption in the 400–530 nm range and relatively large lifetimes is observed by conventional laser flash photolysis. Moreover, with primary amines (methylamine or *n*-hexylamine), the NV radical anion is not observed directly and its existence is inferred through indirect methods. (Preliminary laser flash photolysis experiments [35] of the photoreaction of NV with PhEA in aqueous solution show that the photobehaviour is analogous to that previously reported [31] for methylamine and *n*-hexylamine.) By contrast, in the investigation of the solid ternary NV/PhEA/ β -CD complex by DRLFP, only the photoreduction process is observed, i.e. the formation of the radical anion and photoreduction intermediates, without interference from other competitive processes such as photosubstitution and the formation of σ complexes, despite the fact that photosubstitution products by PhEA are obtained in aqueous solution [29]. This highly selective process in the ternary complexes supports the existence of real inclusion complexes in the solid state in which the selectivity is the result of the constraints imposed by the CD cavity on the included reagents.

In summary, the results presented here show that, provided that interaction between the reactants is possible in solid CD inclusion complexes, the study of such complexes by DRLFP is valuable in the investigation of bimolecular photoinduced reactions, especially when they are difficult to study in solution due to the existence of other competitive processes.

Acknowledgements

Financial support from the DGICYT (Ministerio de Educación y Ciencia of Spain), through project PB93-0895, and from the Generalitat de Catalunya, through project 1995SGR00469, is gratefully acknowledged. We also thank DGICYT for a postdoctoral grant to M.M.

References

- [1] K. Kalyanasundaram, *Photochemistry in Microheterogeneous Systems*, Academic Press, Orlando, 1987.
- [2] V. Ramamurthy (Ed.), *Photochemistry in Organized and Constrained Media*, VCH Publishers, New York, 1991.

- [3] V. Ramamurthy, R.G. Weiss, G.S. Hammond, *Adv. Photochem.* 18 (1993) 67.
- [4] V. Ramamurthy, R.G. Weiss, G.S. Hammond, *Adv. Photochem.* 18 (1993) 69.
- [5] M.L. Bender, M. Komiyama, *Cyclodextrin Chemistry*, Springer-Verlag, New York, 1977.
- [6] W. Saenger, *Angew. Chem., Int. Ed. Engl.* 19 (1980) 344.
- [7] G. Wenz, *Angew. Chem., Int. Ed. Engl.* 33 (1944) 803.
- [8] V. Ramamurthy, D.F. Eaton, *Acc. Chem. Res.* 21 (1988) 300.
- [9] D.F. Eaton, *Tetrahedron* 43 (1987) 1551.
- [10] P. Bortolus, G. Grabner, G. Kohler, S. Monti, *Coord. Chem. Rev.* 125 (1993) 261.
- [11] P. Bortolus, S. Monti, *Adv. Photochem.* 21 (1996) 1.
- [12] W. Chung, N.J. Turro, J. Silver, W.J. le Noble, *J. Am. Chem. Soc.* 112 (1990) 1202.
- [13] S. Monti, L. Flamigni, A. Martelli, P. Bortolus, *J. Phys. Chem.* 92 (1988) 4447.
- [14] M. Barra, C. Bohne, J.C. Scaiano, *Photochem. Photobiol.* 54 (1991) 1.
- [15] M. Sikorski, M. Mir, F. Wilkinson, *Chem. Commun.* (1997) 395.
- [16] M.S. Syamala, V. Ramamurthy, *Tetrahedron* 44 (1988) 7223.
- [17] M.S. Syamala, B.N. Rao, V. Ramamurthy, *Tetrahedron* 44 (1988) 7234.
- [18] V. Ramamurthy (Ed.), *Photochemistry in Organized and Constrained Media*, VCH Publishers, New York, 1991, Chapter 7.
- [19] M. Koshioka, H. Mizuma, K. Imagi, N. Ikeda, H. Fukumura, H. Masuhara, H. Kryschi, *Bull. Chem. Soc. Jpn.* 63 (1990) 3495.
- [20] M. Barra, J.C. Scaiano, *Photochem. Photobiol.* 62 (1995) 60.
- [21] J.L. Bourdelande, J. Font, R. González-Moreno, *J. Photochem. Photobiol. A: Chem.* 94 (1996) 215.
- [22] R.W. Kessler, F. Wilkinson, *J. Chem. Soc., Faraday Trans. 1* 77 (1981) 309.
- [23] F. Wilkinson, C.J. Willsher, *Tetrahedron* 43 (1987) 1197.
- [24] F. Wilkinson, G. Kelly, in: J.C. Scaiano (Ed.), *Handbook of Organic Photochemistry*, Vol. 1, CRC Press, Boca Raton, FL, 1989, pp. 293–314.
- [25] M.C. Gonzalez, A.R. McIntosh, J.R. Bolton, A.C. Weedon, *J. Chem. Soc., Chem. Commun.* (1984) 1138.
- [26] E. Adar, Y. Degani, Z. Goren, I. Willner, *J. Am. Chem. Soc.* 108 (1986) 4696.
- [27] H. Yonemura, H. Nakamura, T. Matsuo, *Chem. Phys. Lett.* 155 (1989) 177.
- [28] H. Murai, Y. Yamamoto, Y. J. Haya, *Can. J. Chem.* 69 (1991) 1643.
- [29] M. Mir, J. Marquet, E. Cayón, *Tetrahedron Lett.* 33 (1992) 7053.
- [30] M. Mir, J. Marquet, in preparation.
- [31] A.M. Van Eijk, A.H. Huizer, C.A.G.O. Varma, J. Marquet, *J. Am. Chem. Soc.* 111 (1989) 88.
- [32] K. Harata, *Bull. Chem. Soc. Jpn.* 50 (1977) 1416.
- [33] R.J. Bergeron, M.A. Channing, *J. Am. Chem. Soc.* 101 (1979) 2511.
- [34] C.J. Easton, S.E. Lincoln, D.M. Schliebs, *Chem. Commun.* (1995) 1167.
- [35] M. Mir, Ph.D. Thesis, Universitat Autònoma de Barcelona, 1995.
- [36] Y.L. Chow, J. Michon, P. Michon, C. Morat, A. Rassat, *Tetrahedron Lett.* 33 (1992) 3315.
- [37] D. Dopp, *Top. Curr. Chem.* 55 (1975) 49.
- [38] A.N. Frolov, N.A. Kuznetsova, A.V. El'tsov, *Russ. Chem. Rev. (Engl. Trans.)* 45 (1976) 1024.
- [39] N. Levy, M.D. Cohen, *Mol. Photochem.* 8 (1977) 155.
- [40] Y.L. Chow, *The Chemistry of Amino, Nitroso and Nitro Compounds and their Derivatives*, Wiley, New York, 1982, Part 1, Supplement F, Chapter 6.
- [41] R. Nakagaki, K. Mutai, *Bull. Chem. Soc. Jpn.* 69 (1996) 261.
- [42] R.W. Yip, D.K. Sharma, R. Giasson, D. Gravel, *J. Phys. Chem.* 88 (1984) 5770.
- [43] C.A.G.O. Varma, F.L. Plantenga, F.L. Huizer, J.P. Zwart, Ph. Bergwerf, J.P.M. van der Ploeg, *J. Photochem.* 24 (1984) 133.

- [44] L.V. Vieira Ferreira, J.C. Netto-Ferreira, I.V. Khmelnski, A.R. Garcia, S.M.B. Costa, *Langmuir* 11 (1995) 231.
- [45] A.B. Berinstein, M.K. Whittlesey, J.C. Scatano, *ACS Symp. Ser.* 531 (1993) 111.
- [46] J.S. Brinen, B. Singh, *J. Am. Chem. Soc.* 93 (1971) 6623.
- [47] A. Cantos, J. Marquet, M. Moreno-Mañas, A. Castelló, *Tetrahedron* 44 (1988) 2607.
- [48] A. Cantos, J. Marquet, M. Moreno-Mañas, A. González-Lafont, J.M. Lluch, J. Bertrán, *J. Org. Chem.* 55 (1990) 3303.
- [49] W.J. Leigh, M.S. Workentin, D. Andrew, *J. Photochem. Photobiol. A: Chem.* 57 (1991) 97.
- [50] M. Barra, C. Bohne, J.C. Scatano, *J. Am. Chem. Soc.* 112 (1990) 8075.
- [51] H.L. Casal, J.C. Scatano, *Can. J. Chem.* 62 (1984) 628.
- [52] H.L. Casal, J.C. Scatano, *Can. J. Chem.* 63 (1985) 1308.
- [53] R. González-Blanco, J.L. Bourdelande, J. Marquet, *J. Org. Chem.* 62 (1997) 6903.
- [54] A. Sauer, F. Wasgestian, U. Nickel, *Bull. Chem. Soc. Jpn.* 62 (1989) 2688.
- [55] R.K. McMullan, W. Saenger, J. Fayos, D. Mootz, *Carbohydr. Res.* 31 (1973) 37.
- [56] T.W. Panunto, Z. Urbanczyk-Lipkowska, R. Johnson, M.C. Etter, *J. Am. Chem. Soc.* 109 (1987) 7786.
- [57] M.C. Etter, *Acc. Chem. Res.* 23 (1990) 120.
- [58] Y. Ito, S. Asaoka, I. Saito, S. Ohba, *Tetrahedron Lett.* 35 (1994) 8193.