Supramolecular Chemistry

Diffuse Reflectance Laser-flash Photolytic Study of Aromatic Ketones within Calixarene Solid Matrices

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Diffuse Reflectance Laser-flash Photolytic Study of Aromatic Ketones within Calixarene Solid Matrices

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The photochemistry of benzophenone and xanthone within calix[6]arene solid matrices is dominated by their triplet excited states. Triplet decays within hexa-t-butyl-37,38,39,40,41,42-hexaethoxycalix[6]arene host matrices are remarkably simple; while benzophenone triplet decays can be adequately described by a two-exponential function, decays for xanthone (a less flexible ketone than benzophenone) are very well reproduced by a single discrete lifetime model.

The past decades have witnessed an everincreasing number of investigations on photophysical and photochemical processes in organized and constrained media [1,2]. The media studied are many and include organic systems such as micelles, vesicles, microemulsions, and inclusion compounds (complexes) to inorganic systems such as silica, alumina and clays. A major goal of such studies is to utilize the order and restrictions imposed by the host matrix to the reactant molecules (as well as to the reactive intermediates) so as to increase the selectivity of chemical processes, particularly in the solid state where effects can be quite dramatic.

Calixarenes, cyclic oligomers of phenol-formaldehyde condensates are rather recent arrivals in the field of organized and constrained media [3]. Calixarenes are able to form inclusion complexes (with guest molecules occupying intramolecular cavities), as well as clathrates (with guest molecules held in intermolecular voids or channels of the crystal lattice). Most studies and (as a consequence) industrial uses of calixarenes are related to their metal ion complexing properties. The complexation of organic molecules also seems to offer interesting possibilities, and studies are being carried out in solution as well as in the solid state [3].

Time-resolved diffuse reflectance laser-flash photolysis, on the other hand, 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 [4]. Application of spectroscopic techniques of this type should be of value in understanding the effects of solid host matrices on photoinduced processes. To the best of our knowledge, there has not been any report on photochemical properties of organic compounds within calix-

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arene solid matrices. Thus, and in an effort to characterize calixarenes as host media, time-resolved diffuse reflectance laser-flash photolysis techniques have been applied, for the first time, to the study of the photobehavior of aromatic ketones such as benzophenone (BP) and xanthone (XTN) within calix[6]arene matrices (Chart 1) [5].

Laser excitation of BP and XTN within calixarene solid matrices (air equilibrated samples) leads to the readily detectable ketone triplet–triplet (T–T) transient absorption spectra (Fig. 1) [6]. The intensity and kinetics associated with these T–T absorptions depend on the nature (i.e., type of phenolic substituent R) of calixarene employed. Both in the case of BP and XTN the strongest signals are obtained when working with E6 matrices.

The T–T absorption spectrum of XTN is known to be dependent on the polarity of the

media (i.e., $\lambda_{max} = 655$ nm and 615 nm in Cl_4C and 2-propanol, respectively) due to close proximity of n, π^* and π, π^* triplet states [7]. BP triplet, on the other hand, retains n, π^* character under most experimental conditions as a result of a larger energy gap between n, π^* and π, π^* triplet states [8]. Spectra such as those shown for XTN in Figure 1B ($\lambda_{max} = 640$ nm) indicate that XTN senses a sufficiently nonpolar environment within calixarene solid matrices to have a low-lying n, π^* triplet state. Triplet states of the type n, π^* are able to undergo radical-like hydrogen abstractions [9]. Furthermore, in non polar media the reactivity of triplet XTN is about an order of magnitude larger than that of triplet BP [7, 9]. Thus, and taking into account that phenols (and phenol ethers) are known to act as quenchers of carbonyl triplets of the type involved in this study [10], one could anticipate (some) photoinduced hydrogen abstraction. Indeed, short-lived T–T absorptions are particularly observed in the case of XTN/C6. However, (i) no ketyl radical transient absorption could be detected in any case, and (ii) no substrate consumption could be detected after 12 hour-lamp irradiation of solid samples in a Rayonet reactor [11]. Therefore, if any hydrogen abstraction occurs at all, ketyl radicals are decaying rapidly by back hydrogen transfer regenerating the guest
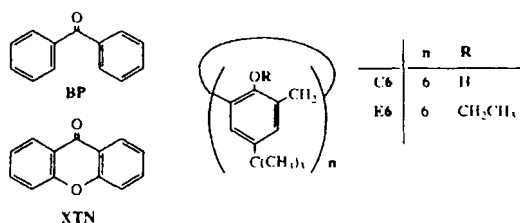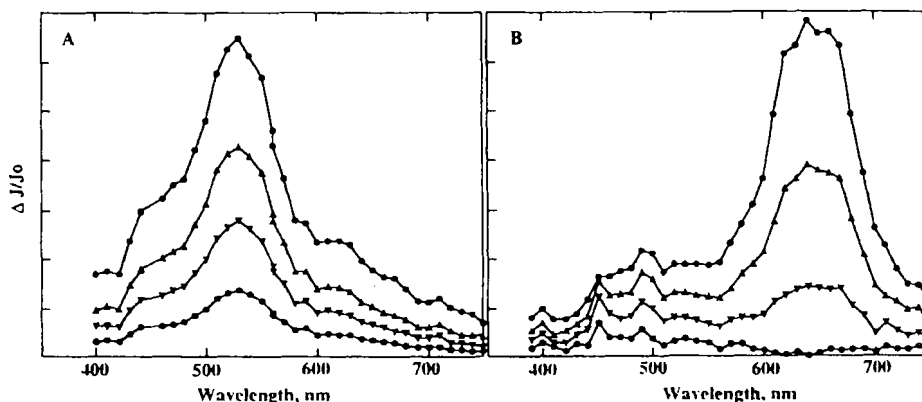

CHART 1

FIGURE 1   Triplet–triplet absorption spectra in hexa-t-butyl-37,38,39,40,41,42-hexaethoxycalix[6]arene solid matrix for (A) benzophenone (obtained within 1.4 μs (•) and 36.2 μs (o) after laser pulse); and (B) xanthone (obtained within 1.0 μs (•) and 32 μs (o) after laser pulse).
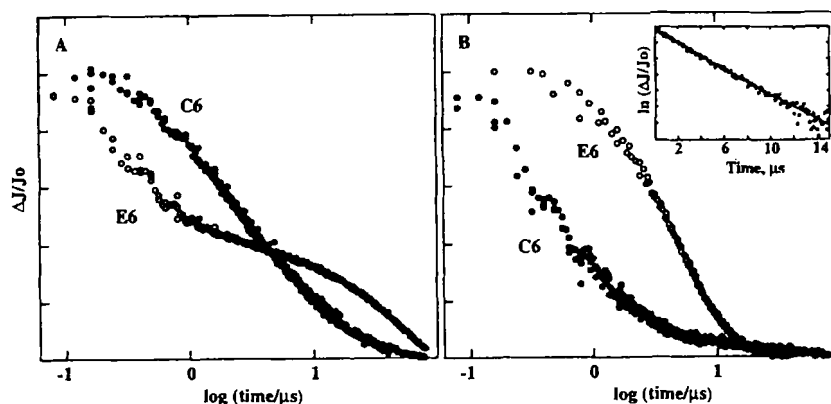
FIGURE 2 Normalized transient decay traces, recorded at different time domains, in p-t-butylcalix[6]arene (C6) and hexa-t-butyl-37,38,39,40,41,42-hexaethoxycalix[6]arene (E6) solid matrices for (A) benzophenone, and (B) xanthone. Inset: linear representation of ln $(\Delta J/J_0)$ vs. time for xanthone triplet decay within E6.

ketones. This observation is not surprising considering the close proximity between chemical partners in the solid samples, and the restrictions imposed by the host matrix on the mobility of the guest species.

For all samples, transient decay traces were recorded on several time scales. Stretched representations (i.e., reflectance changes vs. log (time)) are most convenient for systems involving transient decays covering several orders of magnitude in time scale, as frequently observed in solid system. Typical stretched representations for BP and XTN triplet decays are shown in Figure 2.

The time course of triplet decays can in principle be described as a sum of discrete exponentials:

$$\Delta J/J_0(t) = \sum \alpha_i \exp(t/\tau_i) \qquad (1)$$

where τ_i and α_i are the individual triplet lifetimes and associated preexponential factors of the ith component, respectively. Triplet decays corresponding to E6 solid matrices, much to our surprise, are remarkably simple. While BP triplet decays can be adequately described by two exponential terms (in ca. 1:1 ratio), triplet traces for

XTN (a less flexible ketone than BP) are very well reproduced by a single exponential function (Fig. 2B, inset) [12]. Single or double exponential functions, however, fail to fit triplet decays within C6 matrices.

For comparative purposes, triplet decays (not shown) corresponding to crystalline BP and XTN, and mechanical mixtures of similar concentration as those employed for solvent evaporated samples, were recorded. In the case of crystalline XTN, extremely weak signals are obtained, which could be ascribed as being the result of efficient self-quenching (processs shown to be of relevance in nonpolar media) [7]. Single and double discrete exponential models fail to describe triplet decays in crystalline BP and XTN, which overall are shorter-lived than those observed when using samples isolated by slow solvent evaporation. Also, decay traces corresponding to mechanical mixtures resemble, as expected, those for crystalline ketones. These results clearly indicate that the signals observed with the E6 and C6 solid samples isolated by slow solvent evaporation do not correspond to microcrystalline ketones. Consequently, the changes observed can be taken as indications of inclusion phenomena (either intra or intermolecular), in agreement

with preliminary solid state ^{13}C-NMR observations, as described below.

Recent conformational studies, based on the application of ^{13}C (CPMAS) solid state NMR, indicate that both in the case of C6 an E6, the presence of a single, well-resolved resonance line for the bridging CH_2 groups supports the cone conformation [13]. Transient studies, in turn, show that the phenolic substituent plays quite a significant role in governing triplet decays within these two matrices. While structural details of the samples involved in this study awaits indeed further investigations, preliminary solid state ^{13}C-NMR determinations show no changes in NMR spectra, as expected, when mechanical mixtures are analyzed, in agreement with kinetic decays resembling those for microcrystalline ketones [14]. However, upon incorporation of BP or XTN in either C6 or E6 by slow solvent evaporation, the alkyl region of the solid state spectra of calixarenes is modified (resonance lines move upfield). These changes are a clear indication of ketone/calixarene interactions. Unfortunately, no information that could be correlated with the differences observed in kinetics when comparing BP vs. XTN could be obtained from these spectra.

As already mentioned, a two-exponential function adequately describes BP triplet decay within E6 matrices, whereas a single decay is observed in the case of XTN. The resulting lifetimes (average of three to four determinations) are $\tau_1 = (460 \pm 10)$ ns and $\tau_2 = (42 \pm 6)$ μs for BP, and $\tau = (5.2 \pm 0.5)$ μs for XTN. These values were independent of ketone to calixarene mole ratio. It is quite remarkable the fact that XTN seems to probe a rather 'homogeneous' environment within E6 matrices. Furthermore, the bimodal decay observed in the case of BP could be attributed to two different sites of inclusion within the matrix, or, alternatively, to two different conformations for the more flexible BP. On the other hand, the fact that complex kinetics are observed in the case of C6 matrices would be indicative of a larger diversity of environments

and/or in the conformational structure of guests and host. Crystallographic studies are currently under way in an attempt to obtain sufficient structural information that could correlate with the kinetic results here presented.

Acknowledgments

References

[1] Kalyanasundaram, K. (1987). Photochemistry in micro-heterogeneous systems; Academic Press, Inc.: Orlando.

[2] Ramamurthy, V. (Ed.) (1991). Photochemistry in organized and constrained media; VCH Publishers, Inc.: New York.

[3] Vicens, J. and Böhmer, V. (Eds.) (1991). Calixarenes: a versatile class of macrocyclic compounds; Kluwer Academic Publishers: Dordrecht, The Netherlands, 3.

[4] Wilkinson, F. and Kelly, G. (1989). In Handbook of organic photochemistry; Scaiano, J. C. (Ed.) CRC Press: Boca Raton, 1, 293.

[5] Benzophenone (BDH), xanthone, and p-t-butylcalix[6]-arene (Aldrich) were recrystallized before use. Hexa-t-butyl-37,38,39,40,41,42-hexaethoxycalix[6]arene was prepared according to: Gutsche, C. D. and Lin, L.-G. (1986). Tetrahedron, 42, 1633.

[6] Ketone/calixarene solid samples were prepared by slow solvent evaporation of solutions, in either chloroform or dichloromethane (Omnisolv), containing the corresponding guest compound and calixarene (in 1:1 or 1:2 molar ratio). Laser experiments were carried out using a Nd/YAG laser (Continuum, Surelite I-10) operated at 355 nm (4–6 ns pulses, < 50 mJ/pulse) for excitation. 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. The time-resolved diffuse reflectance laser-flash photolysis system is controlled by a Power Mac 7100/80 computer running LabVIEW 3.1.1 software from National Instruments. Further details on this system are reported elsewhere [Barra, M. and Agha, K. A. (1997). J. Photochem. Photobiol; A: Chem., 109, 293]. All measurements were done at room temperature.

[7] Scaiano, J. C. (1980). J. Am. Chem. Soc., 102, 7747.

[8] Batley, M. and Kearns, D. R. (1968). *Chem. Phys. Lett.*, 2, 423.

[9] Scaiano, J. C. (1973/74). *J. Photochem.*, 2, 81.

[10] Das, P. K., Encimas, M. V. and Scaiano, J. C. (1981). *J. Am. Chem. Soc.*, 103, 4154.

[11] Steady-state irradiations were performed in a Rayonet photoreactor equipped with RPR-3500 lamps from the Southern New England Ultraviolet Co. The samples were contained in quartz cells of the same type used for laser experiments, and were shaken regularly and rotated with a "merry-go-round" apparatus.

[12] Fittings of triplet decay traces were carried out by using the general curve fitting procedure of Kaleidagraph 3.0.5 software from Synergy Software.

[13] Liang, T.-M. and Laali, K. K. (1991). *Chem. Ber.*, 124, 2637–40.

[14] Spectra were recorded at room temperature with a Bruker AMX-500 instrument.