This article was downloaded by:
On: *29 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

Deuterium Isotope Effect on the Complexation of β-Cyclodextrin and Triplet Xanthone in Aqueous Solution

Mónica Barra[a]
[a] Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada

To cite this Article Barra, Mónica(1997) 'Deuterium Isotope Effect on the Complexation of β-Cyclodextrin and Triplet Xanthone in Aqueous Solution', Supramolecular Chemistry, 8: 4, 263 — 266

To link to this Article: DOI: 10.1080/10610279708034944

URL: http://dx.doi.org/10.1080/10610279708034944

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SUPRAMOLECULAR CHEMISTRY, 1997, Vol. 8, pp. 263–266
Reprints available directly from the publisher
Photocopying permitted by license only

© 1997 OPA (Overseas Publishers Association)
Amsterdam B.V. Published under licence under the
Gordon and Breach Science Publishers imprint
Printed in Malaysia

Downloaded At: 15:46 29 January 2011

Communication

Deuterium Isotope Effect on the Complexation of β-Cyclodextrin and Triplet Xanthone in Aqueous Solution

MÓNICA BARRA

Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

(Received 15 July 1996)

The replacement of H_2O by D_2O as solvent leads to a significant decrease in the equilibrium constant for complexation of excited triplet xanthone with β-cyclodextrin, mainly as the result of the decrease in the corresponding association rate constant.

Cyclodextrins (CDs) have been widely used over the past decades due to their ability to form inclusion complexes. While there is a large volume of data available on the complexation equilibrium between various cyclodextrins and numerous substrates, only a couple of reports have been published on solvent isotope effects. In this context, an increase in association equilibrium constants (K_{eq}) when replacing H_2O by D_2O has been observed in the case of complexation of organic dyes and inorganic ions when complexed to α- and β-CDs.[1,2] $K_{eq}(H_2O)/K_{eq}(D_2O)$ ratios varied from 0.67 to 0.89. Due to the small differences in equilibrium constants, the thermodynamic parameters, however, were inconclusive regarding the interactions responsible for the isotope effects.[2]

Kinetic studies, as in the case of thermodynamic studies, can yield information regarding the mechanism of inclusion-complex formation that is not obtainable from equilibrium-constant measurements alone. Cyclodextrins have exchangeable hydrogens and consequently, as in the case of studies of solvent isotope effects in enzyme reactions, it becomes difficult if not impossible to separate solvent from constitutional isotope effects. Studies of H/D isotope effects, however, may lead to some insights into the nature of the association/dissociation process, this being an area relatively unexplored due to the need of very fast experimental techniques. In this communication, application of time-resolved laser flash photolysis to the study of H/D isotope effects on the complexation of β-CD and triplet xanthone is reported.

Xanthone is an aromatic ketone known to form 1:1 inclusion complexes with CDs in aqueous solution.[3] Based on the application of laser flash photolysis techniques it has been shown that,

Downloaded At: 15:46 29 January 2011

following excitation in CD aqueous solutions, xanthone triplet relocates from the cyclodextrin cavity into the aqueous phase.[3] Such relocation was interpreted as being triggered by dipole moment changes between the ground and the triplet states that lead to differences between their association constants and, hence, to a displacement of the equilibrium position. Equilibrium constants for excited triplet xanthone complexed with CDs were later on measured and shown to be, as initially predicted, smaller than those observed for the ground state.[4]

Association equilibrium constants (K_{eq}) for complexation of ground state xanthone with β-cyclodextrin in H_2O and D_2O solutions were determined measuring the decrease in xanthone emission intensity as a function of β-CD concentration, as previously described.[3,5] The values obtained are $(1.11 \pm 0.03) \times 10^3$ M^{-1} and $(1.07 \pm 0.05) \times 10^3$ M^{-1} for H_2O and D_2O, respectively, i.e., the same values within experimental errors and $K_{eq}(H_2O)$ identical to the reported value.

Both in H_2O and D_2O solutions, the shape of the traces obtained upon 355-nm laser excitation of xanthone aqueous solutions containing β-CD depends on the monitoring wavelength, as a result of the changes in the transient spectra as a function of the delay following the laser pulse.[6] The triplet-triplet (T-T) spectra of xanthone shows λ_{max} at *ca.* 605 nm immediately after laser excitation, and at *ca.* 580 nm several hundreds of nanoseconds later. The T-T absorption spectrum of xanthone is known to be dependent on the polarity of the media (e.g., $\lambda_{max} = 655$ nm and 615 nm in Cl_4C and 2-propanol, respectively) due to close proximity of n,π^* and π,π^* triplet states.[7] Thus, the spectral shift observed in the presence of β-CD, which parallels that observed in homogeneous solution when the solvent is changed form a nonpolar to a polar one, is ascribed to the relocation of xanthone triplets from the cyclodextrin cavity to the bulk aqueous phase, as previously reported.[3]

In order to determine association/dissociation rate constants and, consequently, equilibrium constants from transient absorption data, a global compartmental analysis was performed.[8] The transient absorption (ΔA) observed at any monitoring wavelength is given by Equation 1,

$$\Delta A = \varepsilon_{X^*} b [X^*]_t + \varepsilon_{X^* \bullet CD} b [X^* \bullet CD]_t \qquad (1)$$

where ε_{X^*} and $\varepsilon_{X^* \bullet CD}$ are the extinction coefficients for free and complexed triplet xanthone, b is the optical path length, and $[X^*]_t$ and $[X^* \cdot CD]_t$ are the time dependent concentrations of free and complexed triplet xanthone. The expression of these two excited-state concentrations are given by Equations 2 and 3 as a function of the exponential factor $\gamma_{1,2}$ shown in Equation 4:[8]

$$[X^*]_t = \beta_{1,1} \exp(\gamma_1 t) + \beta_{1,2} \exp(\gamma_2 t) \qquad (2)$$

$$[X^* \cdot CD]_t = \beta_{2,1} \exp(\gamma_1 t) + \beta_{2,2} \exp(\gamma_2 t) \qquad (3)$$

$$\begin{aligned} \gamma_{1,2} = {} & -1/2 \{ (k_a[CD] + k_X + k_{X^* CD} + k_d) \\ & \pm ((k_a[CD] + k_X - k_{X^* CD} - k_d)^2 \\ & + 4 k_d k_a [CD])^{1/2} \} \qquad (4) \end{aligned}$$

where β represents pre-exponential factors, k_a and k_d are the association and dissociation rate constants for complexation between triplet xanthone and β-CD, k_X and $k_{X^* CD}$ are the deactivation rate constants for free and complexed triplet xanthone, and [CD] is the free concentration of β-CD.[9]

Substitution in Equation 1 by Equations 2 and 3 leads to:

$$\begin{aligned} \Delta A = {} & (\varepsilon_{X^*} \beta_{1,1} + \varepsilon_{X^* \bullet CD} \beta_{2,1}) b \exp(\gamma_1 t) \\ & + (\varepsilon_{X^*} \beta_{1,2} + \varepsilon_{X^* \bullet CD} \beta_{2,2}) b \exp(\gamma_2 t) \qquad (5) \end{aligned}$$

Decay traces were recorded at 620 nm at different times domains as a function of β-CD concentration. Traces corresponding to each of the β-CD concentration employed were then simultaneously fitted to a double exponential decay using the global lifetime analysis software from Photon Technology International. The lifetimes thus obtained are related to the exponential factors $\gamma_{1,2}$ according to

Downloaded At: 15:46 29 January 2011

$$\gamma_{1,2} = -1/\tau_{1,2} \qquad (6)$$

From Equations 4 and 6 one obtains

$$\begin{aligned} 1/(\tau_1 + \tau_2) &= -(\gamma_1 + \gamma_2) \\ &= k_a[CD] + k_X + k_{X^*CD} + k_d \qquad (7) \end{aligned}$$

Plots of $1/(\tau_1 + \tau_2)$ vs. [CD] are linear (Fig 1), and values of k_a and k_d can be obtained from the slope and intercept. Since the rate of deactivation of free and complex triplet xanthone (i.e., k_X and k_{X^*CD}) is much slower than k_d, the intercept of such plots is indeed k_d.[10] For H_2O as solvent the resulting k_a and k_d values are $(3.0 \pm 0.4) \times 10^8$ $M^{-1}s^{-1}$ and $(9.6 \pm 0.4) \times 10^6 s^{-1}$, respectively. These values are similar to those previously reported, namely, $(2 \pm 1) \times 10^8 M^{-1}s^{-1}$ and $(9.1 \pm 0.7) \times 10^6 s^{-1}$.[11] In the case of D_2O solutions the resulting k_a and k_d values are $(8.8 \pm 0.6) \times 10^7 M^{-1}s^{-1}$ and $(7.6 \pm 0.1) \times 10^6 s^{-1}$, respectively, significantly lower than values in H_2O. Kinetic solvent isotope effects (k_{H2O}/k_{D2O}) range from 0.5 to 6.[12] In this case, k_{H2O}/k_{D2O} ratios of 3.4 and 1.3 are obtained for k_a and k_d, respectively. From these k_a and k_d values the resulting equilibrium constants for complexation of triplet xanthone with β-CD in H_2O and D_2O solutions are (31 ± 5) M^{-1} and (11.6 ± 0.9) M^{-1}, respectively.[13]

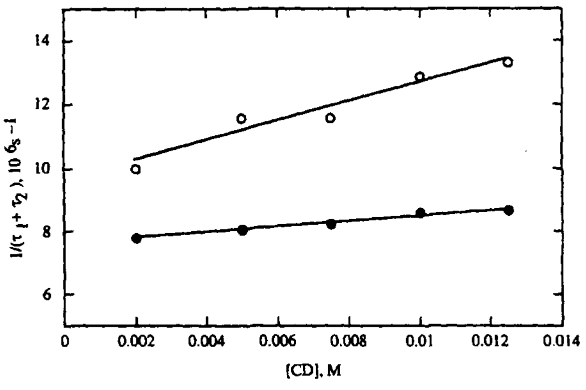

FIGURE 1 Plot of $1/(\tau_1 + \tau_2)$ as a function of total b-CD concentration for triplet xanthone in (O) H_2O and (●) D_2O.

Several intermolecular interactions are responsible for the complexation with native cyclodextrins: hydrophobic interactions, van der Waals forces and hydrogen bonding being typical.[14] On inclusion within the CD cavity the guest molecule must expel the ("activated") water molecules already present in it and strip off its own hydration sphere. Solvent reorganization and solvation of the guest molecule play significant roles in determining the formation of the resultant inclusion complex. Although the properties of H_2O and D_2O are very similar to each other, D_2O forms stronger hydrogen bonds than H_2O and it is more structured.[12,15] The decrease observed in association/dissociation rate constants is in agreement with the observation that hydrophobic interactions probably dominate in complex formation. More detailed investigations as on which are the dominant driving factors (e.g., solvent reorganization, solute/solvent interactions) are currently in progress.

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.

References

[1] Mu, P., Okada, T., Iwami, N. and Matsui, Y. (1993) *Bull. Chem. Soc. Jpn.* **66**, 1924.

[2] Wang, A.S. and Matsui, Y. (1994) *Bull. Chem. Soc. Jpn.* **67**, 2917.

[3] Barra, M., Bohne, C. and Scaiano, J.C. (1990) *J. Am. Chem. Soc.* **112**, 8076.

[4] Liao, Y., Frank, J., Holzwarth, J.F. and Bohne, C. (1995) *J. Chem. Soc., Chem. Commun.*, 199.

[5] Xanthone (Aldrich) was recrystallized from ethanol. β-CD (Aldrich) was used as received. Water was purified by passage through a Millipore Milli-Q system. D_2O (99.9%) was obtained from Cambridge Isotope Laboratories. Fluorescence spectra were collected by duplicate using a Perkin-Elmer MPF-2A.

[6] Experiments were carried out using a Surelite Nd/YAG laser. Samples were contained in $7 \times 7 mm^2$ quartz cells and were deaerated by bubbling with oxygen-free nitrogen for 20 min. The laser system is controlled by a Power Mac 7100/80 computer operating with LabVIEW 3.1.1 software from National Instruments. This system is similar to that described in ref. 7; details will be published elsewhere.

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

[8] van Stam, J., De Feyter, S., Boens, N. and De Schryver, F. (1995) *J. Chem. Soc., Chem. Commun.*, 2433.

[9] The free concentration of CD is given by its total concentration due to the large excess with respect to the total concentration of xanthone, ca. 3×10^{-5} M.

[10] Lifetimes in water are normally > 3 μs, depending on the quality of degassing.

[11] Liao, Y.; Frank, J.; Holzwarth, J.F. and Bohne, C.; *J. Chem. Soc., Chem. Commun.* **1995**, 2435.

[12] Reichardt, C.; *Solvents and solvent effects in organic chemistry*; VCH Publishers: Cambridge, 1988.

[13] Similar measurements with α- and γ-CDs were not attempted due to the fact that complexes are much weaker than in the case of β-CD and results are not as conclusive (see ref. 3 and 4).

[14] Bender, M.L. and Komiyama, M.; *Cyclodextrin chemistry*; Springer Verlag: New York, 1977.

[15] Némethy, G. and Scheraga, H.A.; *J. Chem. Phys.* **1964**, 41, 680.

Downloaded At: 15:46 29 January 2011