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

On the formation of water-soluble buckminsterfullerene-γ-cyclodextrin complexes

Ágnes Buvári-Barcza[a]; Tibor Braun[a]; Lajos Barcza[a]
[a] Department of Inorganic and Analytical Chemistry, L. Eötvös University, Budapest, Hungary

To cite this Article Buvári-Barcza, Ágnes , Braun, Tibor and Barcza, Lajos(1994) 'On the formation of water-soluble buckminsterfullerene-γ-cyclodextrin complexes', Supramolecular Chemistry, 4: 2, 131 — 133
To link to this Article: DOI: 10.1080/10610279408029872
URL: http://dx.doi.org/10.1080/10610279408029872

SUPRAMOLECULAR CHEMISTRY, Vol. 4, pp. 131–133
Reprints available directly from the publisher
Photocopying permitted by license only

On the formation of water-soluble buckminsterfullerene-γ-cyclodextrin complexes

ÁGNES BUVÁRI-BARCZA, TIBOR BRAUN and LAJOS BARCZA

Department of Inorganic and Analytical Chemistry, L. Eötvös University, Budapest, P.O. Box 123, 1443 Hungary

(Received November 18, 1993)

γ-Cyclodextrin appears to catalyze the reaction of C_{60} with water during reflux and in addition to the water soluble 1:1 and 2:1 complexes (whose stability constants could be estimated as ≥ 4 × 10^2 and ≥ 4 × 10^4, respectively) some (complexed) fullerene derivatives are also formed.

INTRODUCTION

Buckminsterfullerene, C_{60}, is rather poorly soluble in most organic solvents[1,2] and the process of dissolution itself is rather slow (it takes 2 hours[1] but 5[1] or 24[2] hours are recommended for saturation at about room temperature). The temperature dependence of the solubility seems also to be anomalous[3]. Similarly, the solvation interactions must be rather complicated[2] and the composite picture of the appropriate solvents[2] predicts no or infinitesimal solubility in water.

In spite of this fact many researchers are keenly interested in the fullerenes in aqueous solution. As published, C_{60} can be solubilized by inclusion complex formation with cyclodextrins[4-6] or calixarenes[7]. It is rather unusual in host-guest chemistry for inclusion complexes to be formed only after refluxing for several hours,[4,6-7] but the extremely low solubility of buckminsterfullerene in water

$$C_{60}(s) \rightleftharpoons C_{60}(aq) \qquad \ldots 1$$

hinders the common mechanism of complex formation (with cyclodextrin, CD):

$$C_{60}(s) + CD(aq) \rightleftharpoons CD.C_{60}(aq) \qquad \ldots 2$$

and the heterogeneous reaction

$$C_{60}(s) + CD(aq) \rightleftharpoons CD.C_{60}(aq) \qquad \ldots 3$$

is supposedly slow.

As some experience on the inclusion chemistry of CDs has been accumulated in our laboratory, and the data published on complexation of C_{60} are rather contradictory, it seemed that the investigation of the interaction between CDs and C_{60} could prove useful.

Experimental-results

We found no complex formation with γ-cyclodextrin (cyclooctaamylose, γ-CD) at room temperature according to Eq. 3, either in a longer time or by sonication, and our experiments with liquid-liquid partition were also unsuccessful. (The partition between n-hexane and aqueous γ-CD solution was quite promising but fruitless. Benzene or toluene cannot be used as they form stable and insoluble complexes with cyclodextrin[8] and the competing effect is too strong.)

As in the literature experiments[4,6,9], the water soluble C_{60} complex was sought by refluxing the solid sample (~0.1 mg, but always in excess) with a γ-CD solution of different concentrations (8 × 10^{-4} – 3.2 × 10^{-2} M). The spectra of the dissolved substance were recorded with a Perkin-Elmer Lambda 15 UV-VIS Spectrophotometer after different refluxing time, and one of the series is represented in Fig. 1. Using the most reliable data for the maxima and the molar absorptivities of C_{60} (in n-hexane)[10], a slight red shift can be observed, but the change in the ratios of molar absorptivities and in the broadening of the peaks is more expressed. The disappearance of the sharp, small, but very characteristic peak at λ = 408 nm after 16-24 hours of refluxing is also an indication of some chemical change of the original C_{60}.

The relative increase of the absorptivity at lower wavelengths depends not only on the refluxing time but, still more, on the concentration of cyclodextrin. When the ratios of the maxima at 215 and 260 nm after 40 hours of reflux are represented as a function of γ-CD concentration, the more pronounced effect of lower concentrations can well be seen (Fig. 2). The spectra of less concentrated solutions are very similar to those which

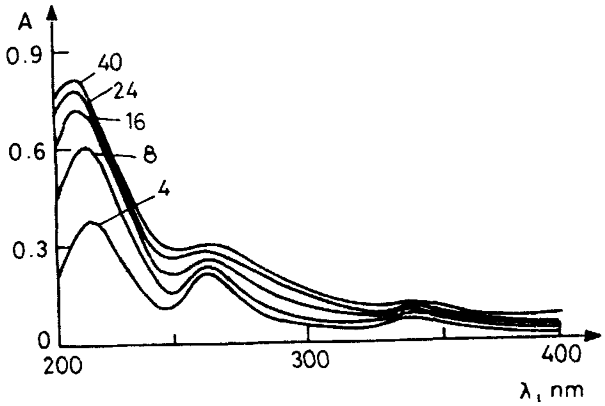

Figure 1 Electronic absorption spectra of C_{60} in 2.00×10^{-3} M γ-CD solution after 4, 8, 16, 24, and 40 hours of reflux.

were assumed to contain further species as some kind of C_{60} clusters[6,4].

The dissolution of C_{60}, i.e. the formation of the inclusion complexes, is of a saturation type as a function of time and its final concentration depends only on the concentration of γ-CD. This is rather strange, because some non-dissolved C_{60} remains as a precipitate in spite of the large excess of CD.

It can be mentioned that 6×10^{-6} M[9], 1×10^{-5} M[4] and 8×10^{-5} M[4] are the highest aqueous concentrations published. We have reached the limit of 1.1×10^{-5} M (regarding the so-called C_{60}).

Similarly, when the concentration of dissolved C_{60} is plotted against the γ-CD concentration (Fig. 3), no linear dependence can be seen, but a system of equilibria appears between two relatively unstable complexes. They are unstable both thermodynamically and kinetically. Without this assumption, Fig. 3 is meaningless, for it proves the presence of two species, but any combination of lower and higher stoichiometric ratios (without conversion of C_{60}) should give a differently shaped curve. It

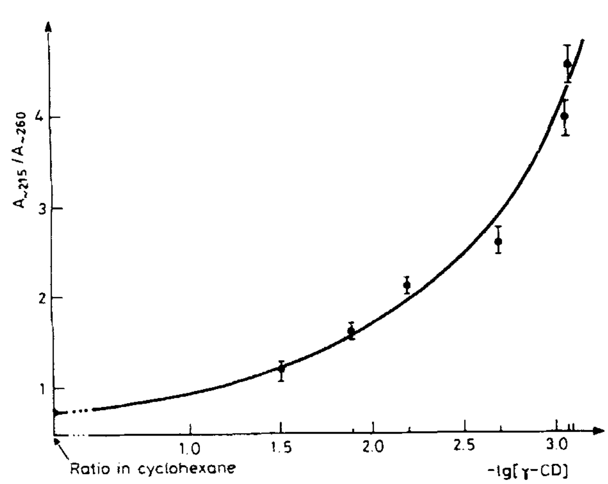

Figure 2 Absorbancy ratios at 215 and 260 nm after 40 hours of reflux as a function of γ-CD concentration.

follows that the complex is relatively stable and does not decompose in the absence of excess γ-CD as stated[4] (i.e. in equilibrium processes), but the C_{60} itself is transformed as a function of time.

Discussion

Most of the inclusion complexes of CD's have a 1:1 host-guest ratio[11], but the 2:1 stoichiometry is also rather common in solution. The presumed structure of the 2:1, i.e. 2 $\gamma\text{-CD.C}_{60}$, complex is represented in Fig. 4, and that of the 1:1 species can be deduced from it. The stability of the 1:1 complex based on Eq. 2, could be characterized by the following stability constant:

$$K_1 = \beta_1 = \frac{[\mathrm{CD.C_{60}}]}{[\mathrm{CD}][\mathrm{C_{60}}]} \qquad \ldots 4$$

where the brackets denote the equilibrium concentrations of complex, CD and C_{60}, respectively, in the aqueous solution.

Similarly, the formation of the 2:1 complex can be characterized as

$$\beta_2 = K_1K_2 = \frac{[\mathrm{2CD.C_{60}}]}{[\mathrm{CD}]^2[\mathrm{C_{60}}]} \qquad \ldots 5$$

or

$$K_2 = \frac{[\mathrm{2CD.C_{60}}]}{[\mathrm{CD}][\mathrm{CD.C_{60}}]} \qquad \ldots 6$$

Unfortunately, the solubility of C_{60} in water, i.e. $[C_{60}]$ is unknown. (The solubility of C_{60} in ethanol, the most polar solvent investigated,[2] is about 10^{-6} M.) The curve in Fig. 3 can be approached with two straight lines with an intersection at about 10^{-2} M CD. Using this concentration, the value of K_2 can be estimated as equal to or greater than 10^2.

Similarly, if we assume that the type and site of interaction of both CDs are equivalent in the $\mathrm{2CD.C_{60}}$ complex (Fig. 4), the ratio of the successive stability constants is determined statistically, i.e.

$$K_1 \geq 4 \times 10^2$$

Comparing these values to the assumed solubility of C_{60}, the estimated stability constants are relatively low and prove the statement that the complexes are thermodynamically unstable. On the other hand, comparing the values to the stability constants in aqueous solution for other CD complexes[8] of aromatic compounds, their order seems rather realistic.

Figs. 1 and 2 prove the decomposition of C_{60} at 100°C after prolonged boiling, representing the kinetic instability. It is well known that the CDs have enzyme-like properties[11], and their complexes are hydrated. This way, the C_{60} and H_2O molecules can exist very close to each other and this may result in a catalysed addition of the solvent at higher temperature.

As the hydration and the domain of the reactive area are different in the 1:1 and 2:1 complexes, both the rate

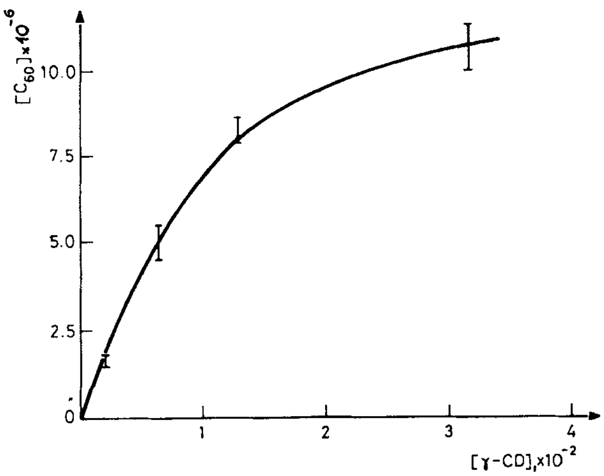

Figure 3 Concentration of C_{60} in aqueous solution as a function of the concentration of CD. (Reflux time: 40 h)

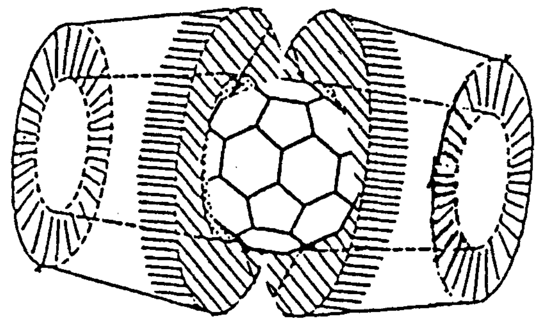

Figure 4 Presumed structure of the 2:1 inclusion complex formed at higher γ-CD concentrations.

and the products of the reactions can be different (as represented in Fig. 3).

The preparation of hydrogenated[12] or hydroxylated[13] fullerenes requires rather aggressive chemical conditions, but the reversible addition of hydroxide[14] (under decolourization!) is a relatively simple reaction. It is worth mentioning that during the electrochemical reduction of C_{60}, the spectrum changes very similarly[15] to that represented in Fig. 1 and the reduced C_{60}^{-} forms an epoxide, $C_{60}O$[16], with water very quickly.

The transformation of C_{60} during reflux is supported by the results of the investigation of C_{60} recovery from the aqueous solution (and they contradict some earlier findings[4]). Theoretically, the C_{60} complex, when contacted with toluene (benzene), should give an insoluble and rather stable CD.toluene complex[8] and a C_{60} solution in the organic phase. In reality, the C_{60} cannot be recovered from a more concentrated solution but is precipitated together with the CD.toluene complex. Almost no C_{60} was recovered from dilute CD solutions.

To fully understand the reaction requires further investigations and we are following our work on these problems of interest to the chemistry of both fullerenes and cyclodextrins.

Acknowledgement

The authors wish to thank the Hungarian OTKA Commission for financial support via research grants Nos. 2277 and 273524. γ-Cyclodextrin was received as a gift from CYCLOLAB (Hungary).

References

1 Sivaraman, N.; Dhamoradan, R.; Kaliappan, I.; Srinivasan, T.G.; Vasudeva Rao, P.R.; Mathews, C.K. *J. Org. Chem.* **1992**, *57*, 6077
2 Ruoff, R.S.; Tse, D.S.; Malhotra, R.; Lorents, D.C. *J. Phys. Chem.* **1993**, *97*, 3379
3 Ruoff, R.S.; Malhotra, R.; Huestis, D.L.; Tse, D.S.; Lorents, D.C. *Nature* **1993**, *362*, 140
4 Andersson, T.; Nilsson, K.; Sundahl, M.; Westman, G.; Wennerström, O. *J. Chem. Soc., Chem. Commun.* **1992**, 604
5 Kutner, W.; Boulas, P.; Kadish, K.M. *J. Electrochem. Soc.* **1992**, *139*, 243C
6 Sundahl, M.; Andersson, T.; Nilsson, K.; Wennerström, O.; Westman, G. *Synthetic Metals* **1993**, *55 – 57*, 3252
7 Williams, R.M.; Verhoeven, J.W. *Rec. Trav. Chim. Pays-Bas* **1992**, *111*, 531
8 Buvári, Á.; Barcza, L. *Acta Chim. Hung.* **1989**, *126*, 455
9 Dimitrijevic, N.M.; Kamrat, P.V. *J. Phys. Chem.* **1993**, *97*, 7623
10 Allemand, P.M.; Koch, A.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarez, M.M.; Anz, S.J.; Whetten, R.L. *J. Am. Chem. Soc.* **1991**, *113*, 1050
11 Szejtli, J. *Cyclodextrin Technology*, Kluwer Academic Publishers, Dordrecht/Boston/London, **1988**.
12 Haufler, R.E.; Conceicao, J.; Chibante, L.P.F.; Chai, Y.; Byrne, N.E.; Flanagen, S.; Haley, M.M.; O'Brien, S.C.; Pan, C.; Xiao, Z.; Billups, W.E.; Ciufolini, M.A.; Hange, R.H.; Margrave, J.L.; Wilson, L.J.; Curl, R.F.; Smalley, R.E. *J. Phys. Chem.* **1990**, *94*, 8634
13 Chiang, L.Y.; Swirczewski, J.W.; Hsu, C.S.; Chowdhury, S.K.; Cameron, S.; Creegan, K. *J. Chem. Soc., Chem. Commun.* **1992**, 1791
14 Naim, A.; Shevlin, P.B.; *Tetrahedron Lett.* **1992**, *33*, 7097
15 Dubois, D.; Kadish, K.M.; Flanagan, S.; Haufler, R.E.; Chibante, L.P.F.; Wilson L.J. *J. Am. Chem. Soc.* **1991**, *113*, 4364
16 Kalsbeck, W.A.; Thorp, H.H. *J. Electroanal. Chem.* **1991**, *314*, 364