Electrochemical Studies of Calixarene-[60]Fullerene Inclusion Processes

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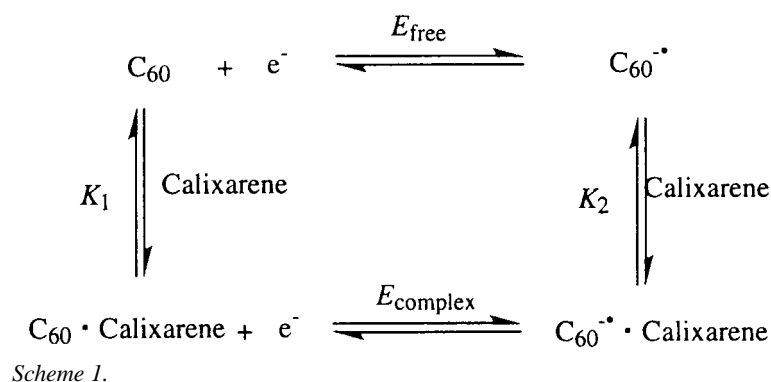
Abstract. [60]Fullerene (C_{60})-calix[n]arene interactions were studied in toluene : MeCN = 10 : 1 (v/v) using an electrochemical method. In the presence of homooxacalix[3]arenes and calix[5]arenes, both E_{pc} and E_{pa} shifted to the negative potential, whereas they were scarcely affected by the addition of calix[4]arenes. The K_2 values electrochemically determined for the association with $C_{60}^{-\cdot}$ are generally smaller than the K_1 values spectroscopically determined for the association with C_{60}. The tendency indicates that the charge-transfer-type interaction is one of the driving forces for C_{60} inclusion.

1. Introduction

In 1994, Suzuki *et al.* [1] and Atwood *et al.* [2] discovered that *p-tert*-butylcalix[8]-arene selectively includes C_{60} in carbon soot and forms the precipitate with a 1 : 1 stoichiometry. This is a very novel and useful purification method to obtain C_{60} in large quantities and a high purity [3] and a doorway to the new marriage of the third generation of inclusion compounds and carbon clusters [4]. It was believed that the origin of selective inclusion stemmed from the conformity of the C_{60} size with the calix[8]arene cavity. However, when this complex was solubilized in solution (e.g., by heating or using good solvents), it was dissociated into each component and no spectroscopic indication of complex formation could be found [4]. This means that this complex can exist stably only in the solid state. More recently, Ikeda *et al.* [5] and Haino *et al.* [6] found that among calix[n]arene homologues, homooxacalix[3]arene, calix[5]arene, and calix[6]arene can include C_{60} even in solution (e.g., toluene). The prerequisites for inclusion are now considered to be a preorganized cone conformation and a proper inclination of the benzene rings [5, 7]. Meanwhile, Bard *et al.* [8] found that the calix[8]arene·C_{60} complex (solid)

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$$C_{60} + e^{-} \underset{E_{free}}{\rightleftarrows} C_{60}^{-\bullet}$$

K_1 | Calixarene K_2 | Calixarene

$$C_{60} \cdot Calixarene + e^{-} \underset{E_{complex}}{\rightleftarrows} C_{60}^{-\bullet} \cdot Calixarene$$

Scheme 1.

embedded in an electroconductive polymer membrane tends to be dissociated when it is electrochemically reduced. This finding suggests that the charge-transfer-type interaction is one of the driving forces for C_{60} inclusion. The above findings suggest the association-dissociation processes as depicted in Scheme 1. The purpose of the present study is to discover whether, or not, reduced C_{60} species are dissociated from calix[n]arenes in solution by using an electrochemical method. Here, for the sake of simplicity, we limit the reduced species to only $C_{60}^{-\bullet}$.

1   **2_nR (R = H, Bu^t)**   **3**
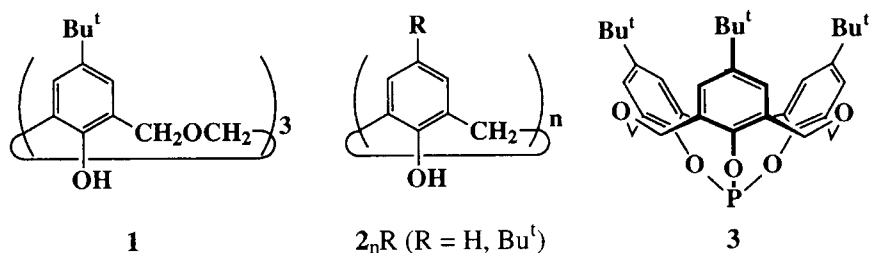
2. Experimental

The electrochemical behavior of C_{60} in the absence and presence of calixarenes has been monitored by cyclic voltammetry (CV). CV was performed on a Windows-driven BAS 100 W electrochemical analyzer. A 3-mm diameter glassy carbon electrode was used as a working electrode. The auxiliary electrode was an Au electrode. Ag/Ag^+ (0.1 M in MeCN/0.1 M Bu_4NPF_6) was used as a reference electrode. All potentials are referenced to the ferrocene/ferrocenium couple (Fc/Fc^+) as the internal standard. All measurements were carried out at room temperature under nitrogen in toluene : MeCN =10 : 1 (v/v) containing 0.1 M Bu_4NPF_6. The values plotted in Figure 2 are the average of three measurements. The error range is shown by the bars.

Table I. Shifts of reduction and oxidation potentials (E_{pc} and E_{pa})[a] and association constants (K_1 and K_2)[b]

Calix[n]arene	ΔE_{pc} /mV	ΔE_{pa} /mV	K_1 /dm^3 mol^{-1}	K_2 /dm^3 mol^{-1}
1	−14	−16	35	13
2$_4$H	−2	−3	0	0
2$_5$H	−16	−2	200	135
2$_5$Bu^t	−16	−17	300	140
3	−13	−8	1600	1040

[a] The error range is ±2 mV. The ΔE values recorded here are those at $[C_{60}] = 5.00 \times 10^{-4}$ mol dm^{-3} and [calix[n]arene]= 2.50×10^{-2} mol dm^{-3} for **1**, **2**$_4$H, and **2**$_5$Bu^t, 2.50×10^{-3} mol dm^{-3} for **2**$_5$H, and 1.00×10^{-3} mol dm^{-3} for **3**. These concentrations are close to the upper limit of the calix[n]arene solubility.
[b] The relative error range is 10%.

Preparation of compounds has been described in: **1** [9], **2**$_4$H [11], **2**$_5$Bu^t, [12], **2**$_5$H [13], and **3** [14].

3. Results and Discussion

3.1. DETERMINATION OF THE K_1 VALUES

The K_1 values for inclusion of C_{60} were estimated in toluene : MeCN = 10 : 1 (v/v) at 25 °C by a conventional spectroscopic method [5]. The results are summarized in Table I. As expected [5, 6] **1**, **2**$_5$H, and **2**$_5$Bu^t showed a moderate affinity, whereas the interaction with **2**$_4$H was not detectable under the present measurement conditions ($[C_{60}] = 5.00 \times 10^{-4}$ mol dm^{-3}, [calix[n]arene] = 0–0.10 mol dm^{-3}). Compound **3** with a phosphorus cap gave a K_1 value (1600 dm^3 mol^{-1}) much larger than those for other calix[n]arenes.

3.2. CYCLIC VOLTAMMETRY MEASUREMENTS

In the absence of calix[n]arenes, the potentials for the one-electron reduction-oxidation processes appeared for C_{60}(5.00×10^{-4} mol dm^{-3}) at $E_{pc} = -1.15$ V and $E_{pa} = -1.02$ V (Figure 1). In the presence of **1** (2.50×10^{-2} mol dm^{-3}), both E_{pc} and E_{pa} shifted to the negative potential by −14 and −16 mV, respectively. These negative shifts were unaffected by a change in the sweep speed (10–100 mV s^{-1}). The negative shift of the E_{pc} implies that C_{60} included in **1** is more difficult to reduce. Provided that the $C_{60^-}.$**1** complex is immediately dissociated into C_{60^-} and **1**, the E_{pa} should be unaffected. The negative shift of the E_{pa} implies,
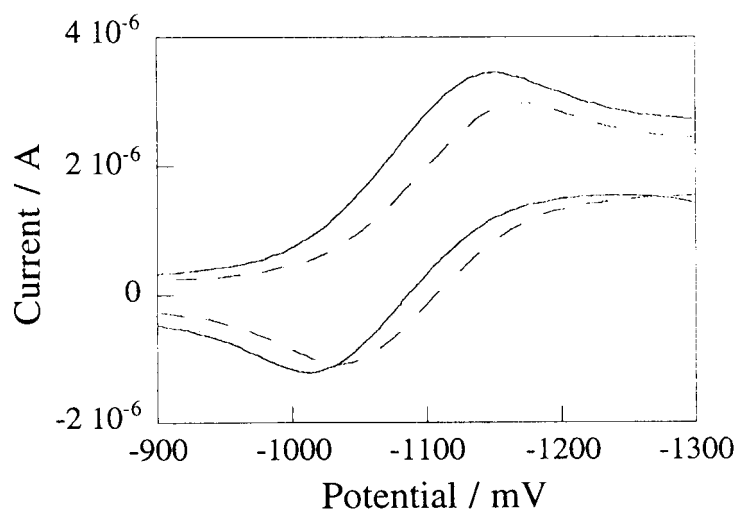
Figure 1. Cyclic voltammograms of 5.00×10^{-4} mol dm^{-3} C$_{60}$: (a) in the absence of **1**, and (b) in the presence of 5.00×10^{-2} mol dm^{-3} **1** in 0.1 mmol dm^{-3} tetrabutylammonium hexafluorophosphate in toluene : MeCN = 10 : 1 (v/v) mixture with ferrocene-ferrocenium ion as the voltage reference at 25 °C and sweep rate 10 mV s^{-1}.

however, that such a dissociation process is not the case and C$_{60^-}$ included in **1** is more easily oxidized. These results support the view that the charge-transfer-type interaction contributes to the association to some extent (as shown by the negative ΔE_{pc}) in addition to other forces, such as the dipole-dipole, $\pi - \pi$, and solvophobic interactions [4–6].

Similar negative changes were also observed for **2$_5$H**, **2$_5$Bu^t**, and **3** which are known to interact with C$_{60}$ by a spectroscopic method (Table I) [4–6, 15]. In contrast, both ΔE_{pc} and ΔE_{pa} were scarcely shifted in the presence of **2$_4$H**, with which no interaction is detectable by the spectroscopic method. The coincidence of the present electrochemical data with the previous spectroscopic data [4, 5] supports our previous conclusion that the prerequisites for C$_{60}$ inclusion in the cavity of calix[n]arenes are the preorganized cone conformation and the proper inclination of the benzene rings.

Both E_{pc} and E_{pa} were determined as a function of calix[n]arene concentrations. Typical examples (for **1** and **2$_4$H**) are shown in Figure 2. From the equation, $E_{\text{free}} = E_{\text{complex}} + (RT/F) \ln(K_1/K_2)$ [16], one can estimate the K_1/K_2 values. Since the K_1 values are determined from spectroscopic studies, the K_2 values for the association of C$_{60^-}$ and calix[n]arenes can be calculated. The results are summarized in Table I. Although it is still difficult to rationalize these results with a clear-cut explanation, the following rationale would be reasonably acceptable: that is, the solvophobic effect would work more strongly on C$_{60^-}$ than on C$_{60}$, whereas, the interaction with the electron-rich calixarene cavity would work more efficiently

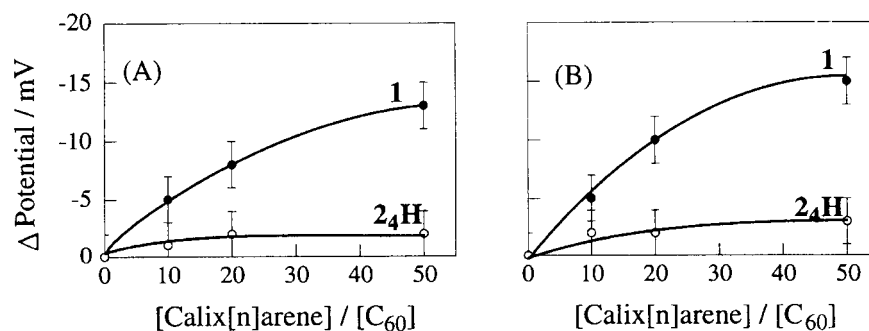*Figure 2.* Plots of the potential difference vs. [calix[n]arene]/[C_{60}]: (A) ΔE_{pc} against the added equivalents of **1** or **2**$_4$H and (B) ΔE_{pa}. C_{60}] = 5.00 × 10^{-4} mol dm^{-3}. The error range is shown by the bars.

on C_{60} than on C_{60^-}. The fact ($K_1 > K_2$) indicates, therefore, that the latter effect related to the charge-transfer-type interaction plays the major role in the present system.

4. Conclusions

The present study demonstrates that the electrochemical data for the C_{60} inclusion are quite complementary to the spectroscopic data, and electrochemically-generated C_{60^-} is not dissociated from the complexes but still interacts with calix[n]arenes more weakly than C_{60} itself. The results indicate that the electrochemical methods are more generally applicable to the investigation of C_{60}-calixarene interaction systems.

This paper is dedicated to the 65th birthday of Professor R. Schmutzler (Technischen Universität Carolo-Wilhelmina, Braunschweig).

References

1. T. Suzuki, K. Nakashima, and S. Shinkai: *Chem. Lett.* 699 (1994).
2. J. L. Atwood, G. A. Koutsantonis and C. L. Raston: *Nature* **368**, 229 (1994).
3. E. Constable: *Angew. Chem., Int. Ed. Engl.* **33**, 2269 (1994).
4. S. Shinkai and A. Ikeda: *Gazz. Chim. Ital.* **127**, 657 (1997).
5. A. Ikeda, M. Yoshimura and S. Shinkai: *Tetrahedron Lett.* **38**, 2887 (1997); A. Ikeda, Y. Suzuki, M. Yoshimura and S. Shinkai: *Tetrahedron* **54**, 2497 (1998).
6. T. Haino, M. Yanase and Y. Fukazawa: *Angew. Chem. Int. Ed. Engl.* **36**, 259 (1997).
7. The X-ray structure of an inclusion complex for a homooxacalix[3]arene was recently reported by K. Tsubaki, K. Tanaka, K. Kinoshita and K. Fuji: *J. Chem. Soc. Chem. Commun.* 895 (1998).
8. D. E. Cliffel, A. J. Bard and S. Shinkai: *Anal. Chem.* **70**, 4146 (1998).
9. B. Dhawan and C. D. Gutsche: *J. Org. Chem.* **48**, 1536 (1983); P. Zerr, M. Mussarabi and J. Vicens: *Tetrahedron* **32**, 1879 (1991).
10. C. D. Gutsche and M. Iqbal: *Org. Synth.* **68**, 234 (1989).

11. S. Shinkai, S. Mori, H. Koreishi, T. Tsubaki and O. Manabe: *J. Am. Chem. Soc*. **108**, 2409 (1986).

12. A. Ninagawa and H. Matsuda: *Makromol. Chem*. **3**, 65 (1982); K. Iwamoto, K. Araki and S. Shinkai: *Bull. Chem. Soc. Jpn*. **67**, 1499 (1994).

13. M. A. Markomitz, V. Janount, D. G. Castner and S. L. Regan: *J. Am. Chem. Soc*. **111**, 8192 (1989).

14. I. Neda, T. Kaukorat and R. Schmutzler: *Main Group Chem. News* **6**, 4 (1998).

15. The electrochemical reduction of C_{60} in the presence of $\mathbf{2}_5Bu^t$ has been already reported. However, it was concluded that the redox potential change of C_{60^-} was scarcely observed: Z. Chen, J. M. Fox, P. A. Gale, A. J. Pilgrim, P. D. Beer and M. J. Rosseinsky: *J. Electroanal. Chem.* **392**, 101 (1995).

16. S. R. Miller, D. A. Gustowski, Z. Chen, G. W. Gokel, L. Echegoyen and A. E. Kaifer: *Anal. Chem.* **60**, 2021 (1988).