



Concerted Diels–Alder reaction between anthracene and C₆₀

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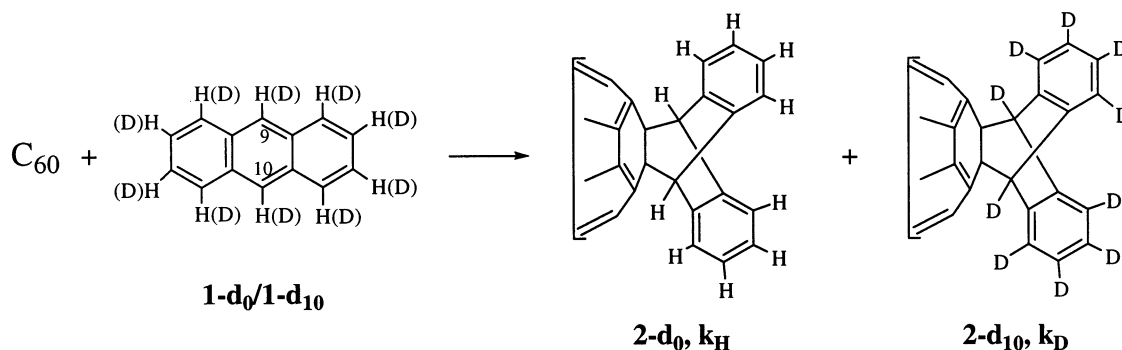
Received 15 November 2000; accepted 29 November 2000

Abstract—The Diels–Alder reaction of anthracene with C₆₀ has been investigated experimentally by using secondary isotope effects. The inverse α -secondary isotope effect in conjunction with the unity value of the β -secondary isotope effect indicates a concerted mechanism for the title reaction. © 2001 Elsevier Science Ltd. All rights reserved.

[60]Fullerene is a reactive electrophile and exhibits a remarkable array of thermal and photochemical reactions. Among the [4+2], [3+2] and [2+2] cycloaddition reactions,¹ the Diels–Alder addition has been widely studied. A large variety of conjugated dienes have been added to C₆₀ in a [4+2] fashion, either directly or after generation in situ. However, most of the work has been focused on product isolation and characterization and little is known about the reaction mechanism. Our recent mechanistic studies of the [2+2] cycloadditions of aryl alkenes,² dienes³ and dienones⁴ to C₆₀ prompted us to also investigate the mechanism of the [4+2] cycloaddition of anthracene to C₆₀.

In this communication we report the α - and β -secondary isotope effects of the thermal [4+2] cycloaddition between anthracenes and C₆₀ and discuss the mechanism derived from the measured isotope effects.

To determine the intermolecular α -secondary isotope effect, C₆₀ (20 mg, 0.027 mmol) and a 1.2% excess of an equimolar mixture of anthracenes **1-d₀/1-d₁₀**⁵ were mixed with naphthalene⁶ and placed in a thick glass tube equipped with a rotaflo valve and magnetic stirrer. The reaction mixture was deoxygenated with argon and heated at 160°C. The reaction was interrupted at various conversions and analyzed by HPLC equipped with a Separon C₁₈ reverse phase column. A 40% yield of the Diels–Alder monoadduct was obtained after 18 h, based on the recovered C₆₀. The reaction mixture was sonicated with pentane to remove the naphthalene solvent and unreacted anthracenes. The fullerene cycloadducts **2-d₀** and **2-d₁₀** (Scheme 1), which are stable at room temperature, were purified by flash column chromatography (SiO₂, hexane/toluene = 9/1) and characterized by ¹H NMR spectroscopy. In the ¹H NMR spectrum, adduct **2-d₀** shows a singlet absorption at 5.80 ppm due to the bridgehead hydrogen atoms and



Scheme 1. Thermal [4+2] cycloaddition reaction of anthracenes **1-d₀/1-d₁₀** with C₆₀.

Keywords: fullerenes; [4+2] cycloaddition; isotope effects; hyperconjugation.

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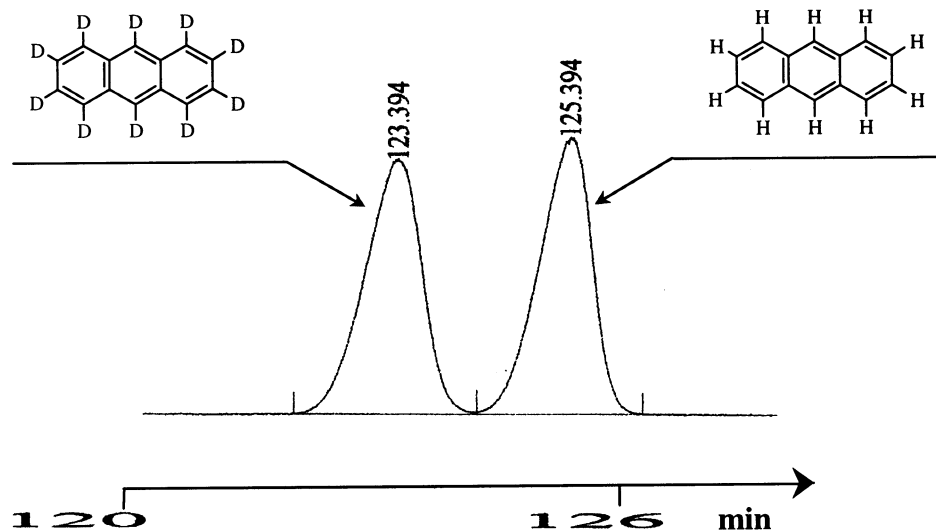


Figure 1. Capillary column gas chromatographic separation of anthracenes **1-d₀** and **1-d₁₀**.

two downfield absorptions at 7.49 and 7.77 ppm, which correspond to the *ortho* and *meta* phenyl hydrogens. The α -secondary isotope effect $k_{\text{H}}/k_{\text{D}}$ is the result of the intermolecular isotopic competition between **1-d₀** and **1-d₁₀** with C_{60} and is proportional to the product ratio **2-d₀**/**2-d₁₀**. Because cycloadduct **2-d₁₀** is fully deuterated, the **2-d₀**/**2-d₁₀** ratio cannot be determined by ^1H NMR spectroscopy. In this case the isotope effect was calculated⁷ from the integration of the gas chromatographic[†] signals of unreacted **1-d₀** and **1-d₁₀** on a 60 meter (5% phenyl) methylpolysiloxane capillary column (Fig. 1). The value of the α -secondary deuterium isotope effect was found to be $k_{\text{H}}/k_{\text{D}} = 0.93 \pm 0.02$ ($k_{\text{H}}/k_{\text{D}} = 0.96 \pm 0.02$ per D).

This result indicates a considerable change in the hybridization of the carbon atoms C_9 and C_{10} (sp^2 to sp^3) in going from the ground state to the transition state along the reaction coordinate. Furthermore, the magnitude of this inverse deuterium isotope effect supports a one-step mechanism for this Diels–Alder reaction. Had it been a stepwise mechanism the α -secondary isotope effect should have been unity or slightly normal.⁸

To verify further the reaction mechanism between anthracene and [60]fullerene the β -secondary isotope effect was determined. In a typical experiment, C_{60} (20 mg, 0.027 mmol) and a stoichiometric amount of an equimolar mixture of **3-d₀**/**3-d₆**⁹ were dissolved in deoxygenated toluene and allowed to react at 0°C. A 45% yield of the Diels–Alder monoadduct was obtained after 1 h, based on the recovered C_{60} . The solvent was evaporated under vacuum and the solid residue was sonicated with pentane to remove the unreacted 9,10-dimethylantracenes. The cycloadducts **4-d₀** and **4-d₆** (Fig. 2) were purified by flash column chromatography

(SiO_2 , C_{60} : hexane, **4-d₀**, **4-d₆**: hexane/toluene = 8/1) and characterized by ^1H NMR spectroscopy. In the ^1H NMR spectrum, the bridgehead methyl hydrogens of adduct **4-d₀** appear at 2.92 ppm, accompanied by two downfield absorptions (7.56 and 7.81 ppm), which correspond to the phenyl hydrogens of cycloadducts **4-d₀** and **4-d₆**. Furthermore, the hydrogen absorptions of the 9,10-dimethylantracenes derived from the facile retro Diels–Alder reaction are clearly shown in the ^1H NMR spectrum (Fig. 2[‡]). Similar decomposition of the C_{60} (9,10-dimethylantracene) cycloadduct has been reported previously.¹⁰ An intermolecular β -secondary isotope effect $k_{\text{H}}/k_{\text{D}} = 0.98 \pm 0.04$ (average) was measured by integration of the methyl hydrogen absorption at 2.92 ppm ($6k_{\text{H}}$) and the phenyl hydrogen absorption at 7.81 ppm ($4k_{\text{H}} + 4k_{\text{D}}$). Moreover, the deuterium isotope effect was calculated⁷ by the integration of the gas chromatography signals of the unreacted 9,10-dimethylantracenes **3-d₀** and **3-d₆** on a 60 meter (5% phenyl) methylpolysiloxane capillary column. The value of the β -secondary isotope effect was found to be $k_{\text{H}}/k_{\text{D}} = 1.00 \pm 0.02$, which is in good agreement with that measured by ^1H NMR spectroscopy.

The results are summarized in Table 1. The unity value of the β -secondary isotope effect in the intermolecular competition of **3-d₀**/**3-d₆** with C_{60} is consistent with the concerted mechanistic pathway. If the cycloaddition reaction proceeded via a dipolar or diradical intermediate, the magnitude of the β -secondary deuterium effect would be expected to be 3–15% per deuterium atom due to the hyperconjugative effect.¹¹

In conclusion, the α - and β -secondary isotope effects measured in the thermal Diels–Alder cycloaddition of anthracenes to C_{60} are consistent with a concerted mechanism.

[†] A control experiment showed that the deuterated anthracene **1-d₁₀** has a shorter GC retention time than the anthracene **1-d₀**.

[‡] Hydrogen absorptions of **3-d₀**/**3-d₆** derived from the retro Diels–Alder of adducts **4-d₀** and **4-d₆**.

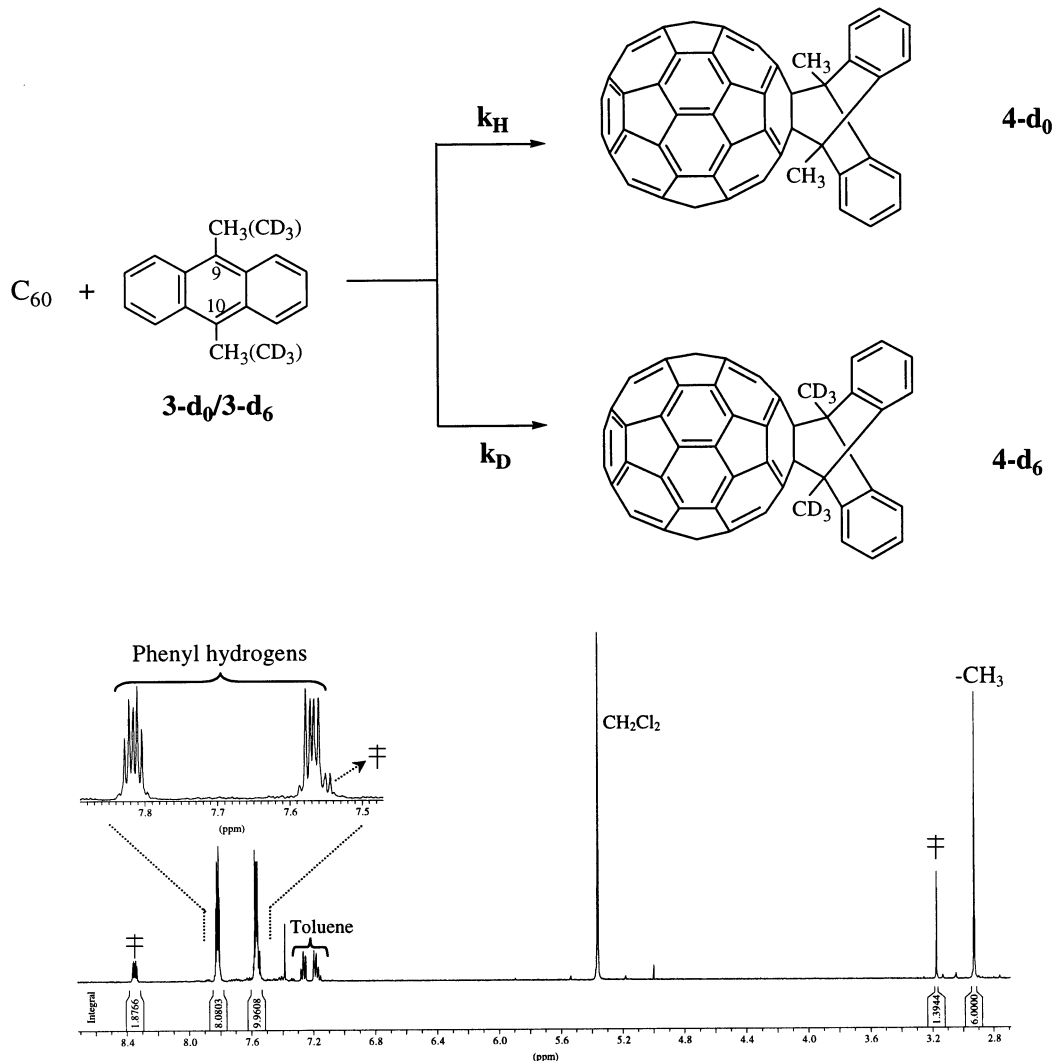


Figure 2. Determination of the β -secondary isotope effect by ^1H NMR spectroscopy.

Table 1. Intermolecular secondary deuterium isotope effects for the Diels–Alder cycloaddition reaction of anthracenes to C_{60}

Type of secondary isotope effect	Substrate	Method of determination	$k_{\text{H}}/k_{\text{D}}$ (average)	$k_{\text{H}}/k_{\text{D}}$ (per D)
α -Secondary	1-d ₀ /1-d ₁₀	GC ^a	0.93±0.02 ^c	0.96±0.02
β -Secondary	3-d ₀ /3-d ₆	^1H NMR ^b	0.98±0.04	0.99±0.04
β -Secondary	3-d ₀ /3-d ₆	GC ^a	1.00±0.02 ^c	1.00±0.02

^a GC analysis was performed on a 60 meter (5% phenyl) methylpolysiloxane capillary column.

^b The value of the isotope effect was determined by ^1H NMR integration of the appropriate signals. The error was $\pm 4\%$.

^c The value of the isotope effect is the average of ten consecutive measurements.

Acknowledgements

We thank Greek Secretariat of Research and Technology (ΠΕΝΕΔ 1999) for financial support and for research fellowship to N.C. Professor G. J. Karabatsos is also acknowledged for valuable comments and discussions.

References

- For reviews on fullerene functionalization, see: (a) Prato, M.; Maggini, M. *Acc. Chem. Res.* **1998**, *31*, 519–26. (b) Diederich, F.; Isaacs, L.; Philp, D. *Chem. Soc. Rev.* **1994**, 243–55. (c) Hirsch, A. *Synthesis* **1995**, 895–913. (d) Hirsch, A. *The Chemistry of Fullerenes*; Georg Thieme

- Verlag: Stuttgart, New York, 1994. (e) Wudl, F. *In Buckminsterfullerenes*; Billups, W. E., Ciufolini, M. A., Eds.; VCH: New York, 1993; Chapter 13. (e) Taylor, R., Ed. *The Chemistry of Fullerenes*; World, Scientific: Singapore, 1995.
- Vassilikogiannakis, G.; Orfanopoulos, M. *J. Am. Chem. Soc.* **1997**, *119*, 7394–7395.
 - Vassilikogiannakis, G.; Chronakis, N.; Orfanopoulos, M. *J. Am. Chem. Soc.* **1998**, *120*, 9911–9920.
 - Vassilikogiannakis, G.; Orfanopoulos, M. *J. Org. Chem.* **1999**, *64*, 3392–3393.
 - Anthracene-d₁₀ is commercially available, 98.5 atom% D (Aldrich Chemical Co.).
 - Komatsu, K.; Murata, Y.; Sugita, N.; Takeuchi, K.; Wan, T. S. M. *Tetrahedron Lett.* **1993**, *34*, 8473–8476.
 - For the calculation of the isotope effect the following expression was used:

$$k_H/k_D = \log(1-H_r/H_i)/\log(1-D_r/D_i)$$
 where H_r , D_r are the amounts of **1-d₀** and **1-d₁₀** that reacted and H_i , D_i are the initial amounts of **1-d₀** and **1-d₁₀**, respectively. Higgins, R.; Foote, C. S.; Cheng, H. *ACS Chem. Ser.* **1968**, *77*, 102–117.
 - Mattson, O.; Westway, K. C. *Adv. Phys. Org. Chem.* **1996**, *31*, 143–248.
 - Spectroscopic data of **3-d₆**: ¹H NMR (500 MHz, CDCl₃): δ 7.55 (dd, $J_1=6.8$ Hz, $J_2=3.2$ Hz, 4H), 8.35 (dd, $J_1=6.8$ Hz, $J_2=3.2$ Hz, 4H). ¹³C NMR (CDCl₃): δ 13.2 (m, due to deuterium atoms), 124.6, 125.3, 128.2, 129.9. MS m/z 212 (M⁺, 100). Compound **3-d₆** was synthesized according to the literature: Duerr, B. F.; Chung, Y. S.; Czarnik, A. W. *J. Org. Chem.* **1988**, *53*, 2120.
 - Lamparth, I.; Maichle-Mössmer, C.; Hirsch, A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1607.
 - Melander, L.; Saunders, Jr., W. H. *Reaction Rates of Isotopic Molecules*; Wiley-Interscience: New York, 1980; p. 174.