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CONTRASTING FREE ENERGIES OF ELECTRON TRANSFER FROM [6] AND [8]ANNULENES TO THEIR PERDEUTERIATED-PER-^{13}C ANALOGUES

Gerald R. Stevenson*, Steven J. Peters, and Kerry A. Reidy,
Department of Chemistry, Illinois State University, Normal, Ill 61761

Abstract: EPR analysis shows that the equilibrium isotope effect upon the equilibrium constant for electron transfer between isotopic isomers is much larger in [6]annulene (i.e. $C_6H_6^{-\cdot} + {}^{13}C_6D_6 = C_6H_6 + {}^{13}C_6D_6^{-\cdot}$) than in the [8]annulene systems (i.e. $C_8H_8^{-\cdot} + {}^{13}C_8D_8 = C_8H_8 + {}^{13}C_8D_8^{-\cdot}$). This is due to the effects of aromaticity.

The most important properties that we can know about any molecular system are its structure and energy, and the addition or subtraction of π electrons to conjugated organic systems can have a most profound effect upon both of these as in the case of [8]annulene,[1a] or to a lesser degree [6]annulene.[1b] The extensive interest in structural perturbations due to π electron addition is accounted for by their importance in understanding conjugation and aromaticity.[1] Since Kekule's original vision of "resonating" structures,[2] there have been a number of empirical and theoretical definitions of aromaticity.[3-4] However, the one tried and true concept that all theoretical models and experimental tests are ultimately compared to is Huckel's 4n + 2 rule.[5] Aromaticity in a Huckel sense is based upon the number of π electrons that exist in a conjugated system. It follows that experimental tests of conjugation and aromatic character might best be based upon the addition or subtraction of π electrons to form ion radicals.[6] Here we wish to propose a direct probe (EPR) into bonding changes upon π electron addition. This probe involves competitions between isotopic isomers of annulenes for a deficient number of electrons. Over the years EPR has proven to be an accurate analytical tool for evaluations of relative concentrations of radicals,[7] and we have made use of this type of measurement applied to annulene isotopic isomers to evaluate the equilibrium constants for the competition reactions.

When a liquid ammonia solution at 205 K under high vacuum containing 0.069 millimoles of [8]annulene and 0.091 millimoles of perdeuteriated-per-^{13}C [8]annulene[8] is reduced with a very molar deficient quantity of freshly distilled Na metal, both anion radicals are generated, and the relative concentrations of the two anion radicals are controlled by the rapid electron transfer equilibrium, reaction 1. EPR analysis of these solutions show that the $[{}^{13}C_8D_8^{-\cdot}]/[{}^{12}C_8H_8^{-\cdot}]$ ratio is close to the $[{}^{13}C_8D_8]/[{}^{12}C_8H_8]$ ratio, and $K_{eq} = 1.17 \pm 0.04$ at 205 K, Figure 1.

$$\Delta G^o = -267 \text{ J/mol at } 205 \text{ K} \qquad (1)$$

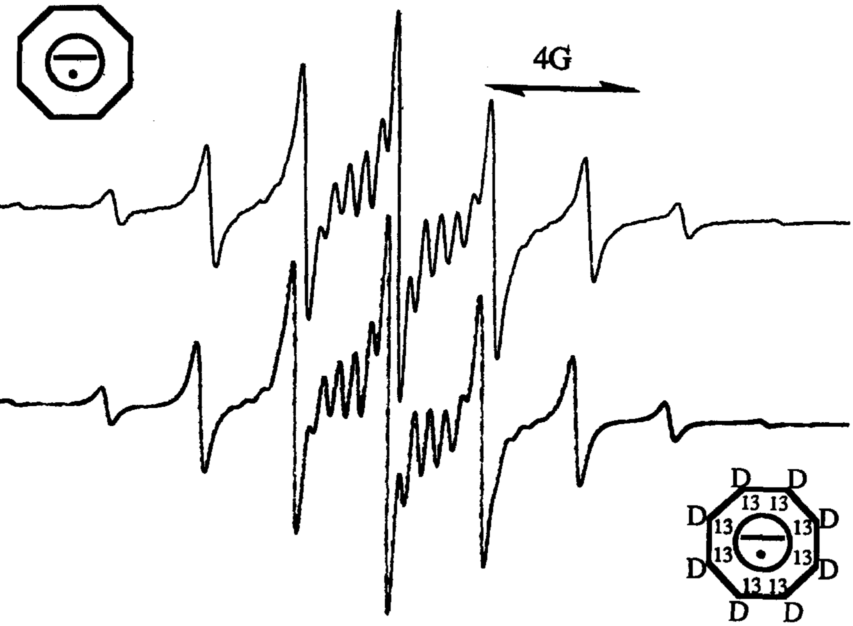
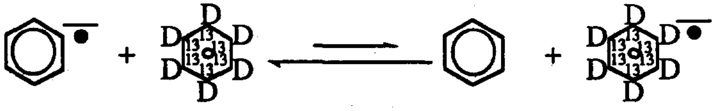


Figure 1. EPR spectrum of a 0.76/1 mixture of C_8H_8 and $^{13}C_8D_8$. The computer simulation (below) was generated by assuming a ratio of $[C_8H_8^{-\cdot}]/[^{13}C_8D_8^{-\cdot}] = 0.65$ ($A_D = 0.51$ G and $A_{^{13}C} = 1.07$ G).

In dramatic contrast, when analogous equilibrium constants were measured for the [6]annulene systems, a very large equilibrium isotope effect was realized, reaction 2. The exposure of a solution containing 0.1578 mmol of $^{13}C_6D_6$ in tetrahydrofuran (THF) containing a molar deficient amount of 18crown6 (0.0254 mmoles) to a potassium mirror under high vacuum results in the formation of the corresponding anion radical. The extent of formation of the anion radical is controlled by the amount of crown ether present. The addition of 0.0141 mmole of $^{12}C_6H_6$ to this solution results in the complete replacement of $^{13}C_6D_6^{-\cdot}$ by $^{12}C_6H_6^{-\cdot}$. However, when only 0.00169 mmoles of $^{12}C_6H_6$ are added to the $^{13}C_6D_6^{-\cdot}$ solution, the EPR signals of both anion radicals can be observed simultaneously at -100 °C, and the relative concentrations of the two are controlled by reaction 2. The resulting EPR spectrum is best simulated using a ratio of $[^{13}C_6D_6^{-\cdot}]/[^{12}C_6H_6^{-\cdot}] = 8.2$. If the solution electron affinities of $^{13}C_6D_6$ and $^{12}C_6D_6$ were identical, this anion radical ratio would have been the same as $[^{13}C_6D_6]/[^{12}C_6H_6]$ or *92.8*. Thus, the K_{eq} for reaction 2 that best fits this experiment is 0.089. From several independent experiments K_{eq} was found to be 0.095 ± 0.008 at 173 K, **ΔG^o = +3.4 kJ/mol.**

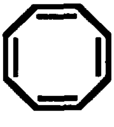


$$\Delta G^o = +3.4 \text{ kJ/mol at } 173 \text{ K} \qquad (2)$$

The equilibrium constants for both reactions 1 and 2 are controlled by the vibrational partition functions,[9,10] which demand that the electron preferentially occupies the isotopic isomer that is least destabilized by its presence. The dramatic contrast in the two isotope effects is due to the fact that the [8]annulene system has 4n π electrons, is nonaromatic, and approaches planar aromatic character upon the addition of nonbonding electrons.[11] On the other hand, [6]annulene has 4n + 2 π electrons, is aromatic, and diverges from aromatic character upon the addition of the antibonding electron. The destabilization of [6]annulene upon electron addition is more extensive for the heavy isotopic isomer.

Similar contrasts in equilibrium isotope effects, but smaller in magnitude, were observed when identical studies were carried out with the [8]annulene and [6]annulene systems that were less extensively isotopically substituted, Table 1 and Figure 2.

Table 1. Free Energy Change and Equilibrium Constant for Electron Transfer (it is assumed that $\Delta H^o = \Delta G^o$, $\Delta S^o = 0$) from the Annulene Anion Radical to the ^{13}C and/or D Isotopically Labeled Annulene.

Annulene	**# of ^{13}C's**	**# of ^{2}H's**	**ΔG^0 (J/mole)**	**K_{eq} (-100 ^{o}C)**	**Reference**
	**0**	**0**	**0.00**	**1.00**	-
	0	**6**	**1937 ± 67**	**0.26 ± 0.02**	**7f**
	6	**0**	**1117 ± 344**	**0.46 ± 0.12**	**7f**
	6	**6**	**3386 ± 65**	**0.095 ± 0.008**	**this work**
	**0**	**0**	**0.00**	**1.00**	-
	0	**8**	**-223 ± 5**	**1.17 ± 0.02**	**this work**
	8	**0**	**34 ± 30**	**0.97 ± 0.03**	**this work**
	8	**8**	**-267 ± 15**	**1.20 ± 0.04**	**this work**

The free energy for reaction 3 will be much greater than 0 when R represents an aromatic system, near

$$R^{-\cdot} + {}^{*}R = {}^{*}R^{-\cdot} + R \qquad (3)$$

zero when R represents a nonaromatic system, and should be much less than zero if R were to represent a symmetric planar antiaromatic (D_{8h}) system. The magnitude of the isotope effect can be controlled by the degree of substitution, Figure 2. In general, an increase in the magnitude of an isotope effect with increased deuterium substitution was predicted by Bigeleisen.[12] In general, the equilibrium constant for reaction 3 should be less than unity whenever bond loosening occurs upon electron addition (the vibrational partition function decreases) and greater than unity whenever bond tightening occurs upon electron addition (the vibrational partition function increases). The test comprises a direct probe into the bonding changes resulting from electron addition.

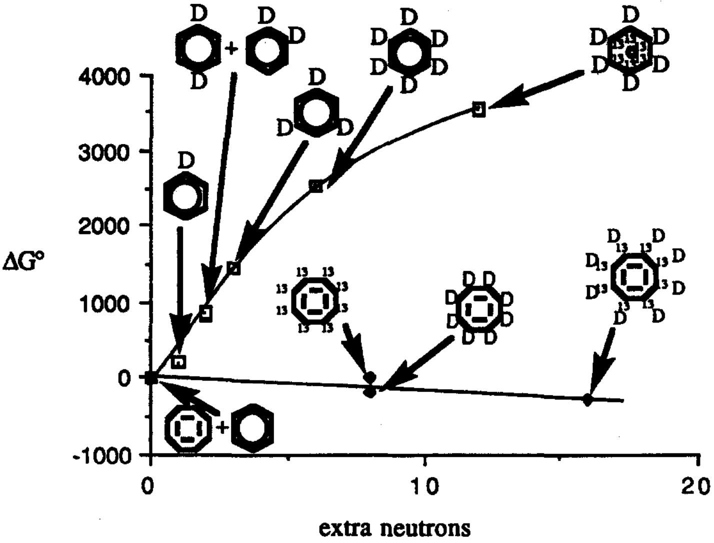


Figure 2.
Plot of ΔG° of electron transfer from the light isotopic isomer to the heavy vs. the number of "extra" neutrons in the form of D's and/or 13C's.

REFERENCES

1. (a) Strauss, H. L.; Katz, T. J.: Fraenkel, G. K. *J. Am. Chem. Soc.* **1963**, 85, 2360. (b) Moore, J. C.; Thorton, C.; Colleir, W. B.; Devlin, J. P. *J. Phys. Chem.* **1981**, 85, 350. (c) Miller, F. A. *J. Chem. Phys.* **1956**, 24, 996.

2. (a) Kekule, A. M. *Annalen* **1872**, CXLII 77. (b) Kekule, A. M. *J. Chem. Soc.* **1872**, X, 612.

3. Hückel, E. Z. *Physik.* **1931**, 70, 20.

4. Hückel, E. Z. *Electrokhim.* **1937**, 43, 752.

5. Stevenson, G. R. in *Molecular structures and Energetics*, Vol. 3, Liebman, J. F.; Greenberg, A. Editors, Chapter 2, VCH Publishers, New York 1986.

6. Zhongxiang, Z.; Parr, R. G. *J. Am. Chem. Soc.* **1989**, 111, 7371.

7. (a) Allendoerfer, R. D.; Papex, P. J. *J. Phys. Chem.* **1972**, 76,1012. (b) Lawler, R. G.; Tabit, C.T. *J. Am. Chem. Soc.* **1969**, 91, 5671. (c) Hirota, N. *J. Phys. Chem.* **1967**, 71 127. (d) Stevenson, G. R.; Alegria, A. E. *J. Phys. Chem.* **1973**, 77, 3100. (e) Kotake, Y.; Jansen, E. G. *J. Am. Chem. Soc.* **1989**, 111, 5138. (f) Stevenson, G. R.; Reidy, K. A.; Peters, S. J.; Reiter, R. C. *J. Am. Chem. Soc.* **1989**, 111, 6578.

8. D_8, $^{13}C_8$, and $D_8{}^{13}C_8$-[8]annulenes are easily synthesized via the Reppe synthesis using appropriately labeled acetylene (MSD Isotopes) see: (a) Reppe, W.; Schlichting, O.; Klager, K.; Toepel, T. *Annalen.* **1948**, 560,1. (b) Lippincott, E. R.; Lord, R. C.; McDonald, R. C. *J. Am. Chem. Soc.* **1951**, 73, 3370.

9. Stevenson, G. R.; Espe, M. P.; Reiter, R. C. *J. Am. Chem. Soc.* **1986**, 108, 5760.

10. Saunders, M.; Laidig, K. E.; Wolfsberg, M. *J. Am. Chem. Soc.* **1989**, 111,8989.

11. (a) Allendoerfer, R. D.; Reiger, P. H. *J. Am. Chem. Soc.* **1965**, 87, 2336. (b) Stevenson, G. R.; Nebgen, M. A. J. *Am. Chem. Soc.* **1986**, 108, 5509.

12. Bigeleisen, J. *J. Chem. Phys.* **1955**, 23, 2264.

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