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Calorimetrically Measurable Enthalpic Isotope Effect

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Calorimetric techniques have revealed that the enthalpy of reaction with water is more exothermic by about 2.2 kcal/mol, for the perdeuteriated naphthalene anion radical ($K^+C_{10}D_8^{\bullet -}(s) + H_2O(liq) \rightarrow {}^1/_2C_{10}D_8H_2(s) + {}^1/_2C_{10}D_8(s) + KOH(aq)$) than it is for the perprotiated system. These results, when coupled with the known enthalpy of electron transfer between naphthalene and its perdeuteriated analogue imply that the heat of hydrogenation of naphthalene decreases by about 1.8 kcal/mol upon perdeuteriation of the naphthalene.

Introduction

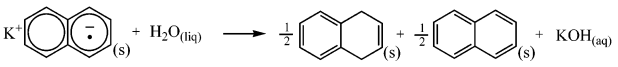
There have been literally thousands of observations of isotope effects, some upon chemical kinetics, the kinetic isotope effect (KIE),[1] and some upon chemical equilibria, the equilibrium isotope effect (EIE).[2] This latter effect can be broken down into entropic and/or enthalpic effects. EIEs can serve as a probe of nonbonding interactions,[2a] yet there have been no direct measurements of nonbonding isotopic heat (enthalpic) effects in chemical reactions. By definition, an enthalpic EIE (qIE) would have to be detected calorimetrically as a perturbation in exo- or endothermicity due to isotopic substitution.

Over a decade ago, we observed a very large, secondary (nonbonding) EIE for the electron transfer between aromatic hydrocarbon anion radicals and their neutral counterparts.[3] For example, at 173 K, reduction of a mixture of benzene and perdeuteriated benzene with potassium metal in THF in the presence of 18-crown-6 was found to favor formation of $C_6H_6^{\bullet -}$ over $C_6D_6^{\bullet -}$ by a factor of 3.85.[4e] The equilibrium constant for the reaction $C_6H_6^{\bullet -} + C_6D_6 \rightleftarrows C_6H_6 + C_6D_6^{\bullet -}$ is 0.26 at 173 K, which corresponds to a 0.47 kcal/mol smaller solution electron affinity for C_6D_6 than for C_6H_6. This should be reflected quantitatively in the enthalpy of electron transfer. B3LYP/6-31+G* density functional calculations reproduce this experimental measurement.[4]

Similarly to the situation with the benzene system, when mixtures of naphthalene and perdeuteriated naphthalene were partially reduced with potassium metal in THF, the resulting EPR spectra indicated that the solution electron affinity (EA) of the isotopically light material is larger than that of the heavy isotopic isomer; see reaction 1.[3g,h] Since that time, the deuterium effect upon solution EA has also been observed via electrochemical techniques,[5] and an analogous effect for cation radicals has been noted.[6]

(1)

At −120 °C, the equilibrium constant for electron transfer between the two ion pairs in reaction 1, determined from the relative EPR intensities of the two anion radicals ($C_{10}H_8^{\bullet -}$ and $C_{10}D_8^{\bullet -}$), in equilibrated mixtures, was reported to be 0.26. This corresponds to a $\Delta G°$ of 410 cal/mol for reaction 1.[3a,h] Because there is no reason for an entropic contribution to $\Delta G°$, it should (in principle) be possible to observe a very small difference in heat release from reactions involving these two isotopic isomers ($K^+C_{10}H_8^{\bullet -}$ and $K^+C_{10}D_8^{\bullet -}$). Here we report a measurable difference in the heat released by the well-known Birch reduction (reaction 2) of naphthalene and of its perdeuteriated analogue. This enthalpic effect is small, but it implies a rather large isotope effect upon the enthalpy of hydrogenation ($\Delta H°_{H_2}$).



(2)

Previously, we have made use of the Birch reduction for the experimental determination of crystal lattice energies for organic anion radicals.[7] The method involves the measurement of the heat of reaction of the solid anion radical salt with water (reaction 2) to produce the neutral hydrocarbon, hydrogenated hydrocarbon, and aqueous alkali metal hydroxide.[7] Crushing thin-walled evacuated bulbs, under water, containing the solid salts of the naphthalene anion radical, results in a rise in the temperature of a calorimeter due to reaction 2. Plots of the rise in the temperature of the calorimeter vs the amount of anion radical salt in the bulbs are linear, and the slopes of the lines are proportional to the enthalpies of the reactions.[7] As our calorimetric techniques and instrumentation improved, we were motivated to attempt to directly measure the "heat content" differences due to the number of neutrons in the organic substrates.

The isotope effect upon the electron transfer between $C_{10}H_8$ and $C_{10}D_8$ (reaction 1) is well explained in terms of zero point energy (ZPE) effects,[3,4] eq 3 (cation effects neglected),[3b] where

$$K_{eq} = \frac{\left(\prod_{i=1}^{i=48} e^{-\epsilon_i/2kT}\right)_{C_{10}D_8^{\bullet -}} \left(\prod_{i=1}^{i=48} e^{-\epsilon_i/2kT}\right)_{C_{10}H_8}}{\left(\prod_{i=1}^{i=48} e^{-\epsilon_i/2kT}\right)_{C_{10}H_8^{\bullet -}} \left(\prod_{i=1}^{i=48} e^{-\epsilon_i/2kT}\right)_{C_{10}D_8}} \qquad (3)$$

the values for ϵ_i represent the 48 vibrational eigenvalues for each of the four species involved in reaction 1. The situation is simplified by the absence of an entropic contribution, $\Delta G° = \Delta H°$.[3,4] Nevertheless, the very small reaction enthalpy (<1 kcal/mol) and the cumulative errors in the 192 eigenvalues along

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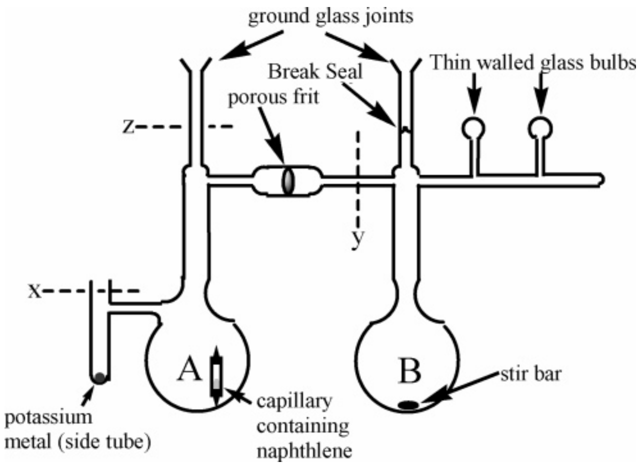


Figure 1. Apparatus used to fill the thin walled glass bulbs with solid naphthalene (or perdeuteriated naphthalene) anion radical salt.

with lattice effects render theoretically predicted equilibrium constants imprecise. The calorimetric measurements described here indicate that a significant zero point energy enthalpic effect also exists in the transfer of hydrogen between $C_{10}H_8$ and $C_{10}D_8$.

Experimental

Sample Preparation. The reductions of naphthalene and perdeuteriated naphthalene were performed in a manner that is analogous to that previously described.[7] A capillary tube was charged with 100.0−130.0 mg of naphthalene or perdeuteriated naphthalene, sealed, and placed in bulb A (Figure 1).

An excess of potassium metal was then placed inside the small side tube, and the top was sealed at point x. The apparatus was attached to a vacuum line using the ground glass joint connected to bulb A. When the entire apparatus was evacuated, the potassium metal was distilled into bulb A, and the side tube was sealed from the rest of the apparatus. Approximately 50 mL of THF was distilled into bulb A, and the entire apparatus was separated from the vacuum line (sealed at point z). The apparatus was then agitated so as to break the capillary containing the naphthalene or perdeuteriated naphthalene. The naphthalene solution was exposed to the freshly distilled potassium metal mirror, resulting in the reduction of the naphthalene to its anion radical. The solution was left in contact with the potassium metal for several hours to ensure that the naphthalene was fully reduced. The resulting anion radical solution was poured through the porous frit into bulb B. The porous frit prevented any solid potassium metal from getting into bulb B. Bulb A was rinsed several times by distilling THF from bulb B back into bulb A and then pouring it back again to bulb B. When all of the naphthalene anion radical had been transferred into bulb B, the THF was again distilled back into bulb A by cooling bulb A with an ice−water bath, with stirring to reduce bumping.

When the vast majority of THF solvent was distilled into bulb A, bulb A (along with the porous frit) was separated from bulb B at point y. Bulb B was connected to the vacuum line, and the break seal was broken (with a magnetic bar). The naphthalene anion radical in bulb B was then left exposed to high vacuum for several hours to ensure complete removal of the THF. Bulb B, with the small bulbs attached, was then sealed from the vacuum line just below the break seal. The "dry" naphthalene anion radical solid salt was then poured into the small, thin calorimeter bulbs. The magnetic stir bar could be used to dislodge salt adhering to the glass walls. The calorimeter bulbs were filled with varying amounts of anion radical salt and sealed from the apparatus. The evacuated calorimeter bulbs, charged with the naphthalene anion radical salt, were broken under water inside the calorimeter cell, Figure 2.

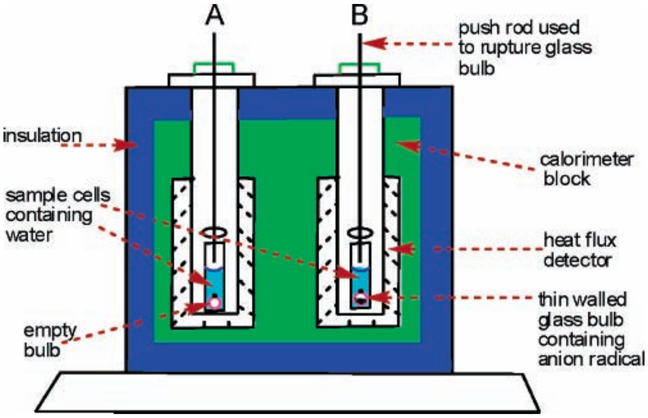


Figure 2. Cut-away block diagram of the calorimeter showing the relative cavity positions. Temperature differences were determined as heat flux of cell B vs cell A.

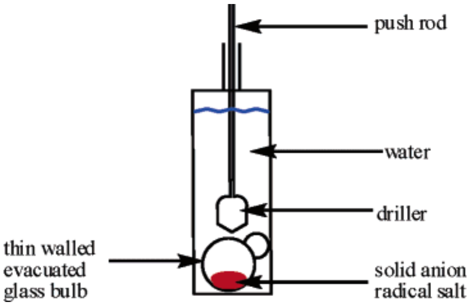


Figure 3. Inside view of the sample cell containing a charged bulb of solid naphthalene (or perdeuteriated naphthalene) anion radical potassium salt (red). The twin cell is the same, except that the evacuated glass bulb is empty.

The thin-walled evacuated glass bulbs, containing either the solid salt $K^+C_{10}H_8^{\bullet-}$ or $K^+C_{10}D_8^{\bullet-}$ were placed into one of the sample cells of a dual cell calorimeter (Figure 2), and empty bulbs were placed in the other cell. The sample cells were then filled with 4.00 mL of water. After thermal equilibrium was established, both bulbs were broken simultaneously and the temperature difference between the two heat flux detectors was monitored with a PC. Experiments were performed with the charged calorimeter bulb in cell A and an evacuated bulb in cell B and visa versa. It should be noted that because the C 80 calorimeter electronically measures heat flux differences by the subtraction of the reference cell from the sample cell, heat spikes are obtained from one arrangement, and heat dips are obtained from the other arrangement.

The bulb's tendency to float to the top of the water inside the cell was circumvented by lowering the driller and pinning the bulb to the bottom of the cell. This ensured that the entire bulb was under water when the bulb was broken with the driller (see Figure 3). The system was considered to be equilibrated when the computer data displayed a horizontal plot of heat flux difference between the sample and reference cells versus time. After a 4 min initial baseline, at equilibrium, was obtained, the drillers in both cells were pushed down rupturing the two calorimeter bulbs simultaneously.

When the bulbs were broken, a heat spike or heat dip resulted due to the enthalpy of the Birch reduction of the naphthalene anion radical. The heat produced due to the exothermic Birch reduction generates a greater amount of heat flux from the

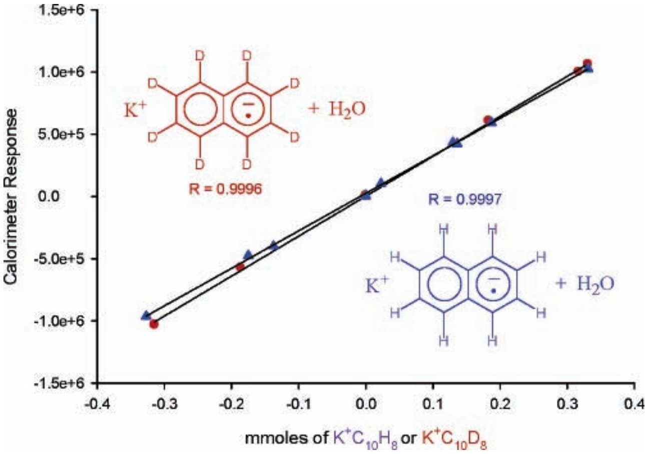


Figure 4. Plot of the heat generated in the calorimeter in arbitrary units (“bytes”) vs the millimoles of solid anion radical salt, determined by titration of product mixtures, in the A cell (negative values) or the B cell (positive values). The red circles represent data for the perdeuteriated system and the blue triangles for the perprotiated system.

corresponding cell to the calorimetric block than the heat flux generated by the twin cell. This heat flux is monitored as a digital signal in the CPU. The area under the resulting curve is a representation of the amount of heat that was generated by the Birch reduction. The heating curves obtained were integrated. Computer output included integrated plots, baseline extrapolations, statistical analysis, and the amount of heat, *q*.

The reaction mixture (consisting of H_2O, KOH, naphthalene, and dihydronaphthalene) were poured out of the cell, which was washed several times with distilled H_2O to ensure total transfer of the aqueous KOH. These solutions were then titrated with 0.010 M HCl. The Birch reduction of naphthalene results in a 1:1 mole ratio of KOH and naphthalene. Therefore, the number of moles of (original) naphthalene anion radical was determined by titrating the number of moles of KOH that was present in solution.

All experiments were performed with the Setaram Astra C 80 Heatflux Calorimeter with amplifier and C 80 Membrane Mixing Cells purchased from Astra Scientific International, Inc. The naphthalene was purchased from Eastman Kodak Co. and the 99% isotopically pure perdeuteriated naphthalene was purchased from Cambridge Isotope Laboratories. The 0.010 M HCl solutions were prepared by dilution of 0.100 M HCl solutions which were purchased from Fisher Scientific Company. The titrations were performed using a Corning pH meter 120 with a Corning General Purpose Combination Electrode. The “raw data”, which are plotted in Figure 4, are shown in Table 1.

The temperature flux was monitored in arbitrary computer units (“bytes”). The rise in temperature was proportional to the difference in the amount of sample in the two cells (A and B). The bulb in one cell was empty, and the computer indicated a negative temperature flux, if the filled bulb was in cell A.

Results and Discussion

Crushing the thin-walled evacuated bulbs containing either the solid salt $K^+C_{10}H_8^{\bullet-}$ or $K^+C_{10}D_8^{\bullet-}$ resulted in a rise in the temperature of the calorimeter due to reaction 4 or 5. Plots of the heat flux (in computer bytes) of the calorimeter vs the amount of anion radical salt in the bulbs are linear (Figure 4), and the slope of the line is proportional to the enthalpy of the reaction. We hoped to detect a very small signal (difference) in thermal output from the perdeuteriated relative to the perprotiated system (reaction 4 vs 5). We were, however, surprised to see a difference in the slopes of the lines, shown in Figure 4, corresponding to about 2200 cal/mol.

TABLE 1: Millimoles of the Anion Radical Salt (Obtained via Titration) and the Resulting Heat Flux (in Arbitrary Units)[a]

$K^+C_{10}H_8^{\bullet-}$	heat flux	$K^+C_{10}D_8^{\bullet-}$	heat flux
0.0225	103870	0.3310	1063500
0.0000	1080.8	0.3170	999490
0.1360	423770	−0.1860	−572580
−0.1375	−398660	0.1830	608750
−0.3270	−961040	−0.3145	−1031400
0.1870	594390	0.0000	8261.70
0.1300	432920		
0.3308	1028520		
−0.1750	−474120		

[a] The negative numbers refer to cell B and the positive numbers refer to cell A. The two resulting lines (Figure 4) do not cross at exactly 0,0 due to cell bias.

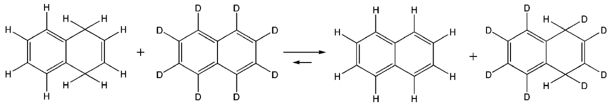
$$K^+C_{10}D_8^{\cdot-}(s) + H_2O(liq) \rightarrow {}^1/_2C_{10}D_8H_2(s) + {}^1/_2C_{10}D_8(s) + KOH(aq) \quad (4)$$

$$K^+C_{10}H_8^{\bullet-}(s) + H_2O(liq) \rightarrow {}^1/_2C_{10}H_{10}(s) + {}^1/_2C_{10}H_8(s) + KOH(aq) \quad (5)$$

The response of the calorimeter (monitored by a PC) to reaction 5 was found to be $(3.040 \pm 0.037) \times 10^6$ bytes/mol, which corresponds to the known −39.1 kcal/mol enthalpy for reaction 5.[3e] The response of the calorimeter produced by the reaction involving the perdeuteriated anion radical was found to be $(3.210 \pm 0.032) \times 10^6$ bytes/mol, which corresponds to an enthalpy for reaction 4 that is 2.19 ± 0.41 kcal/mol more exothermic than it is for reaction 5. The use of the law of Hess, with the assumption (see below) that reaction 1 is enthalpically the same in the solid state as it is in solution, shows that $\Delta H°_{H_2}$ of perdeuteriated naphthalene is more exothermic than it is for naphthalene by more than a kcal/mol.

When mixtures of $C_{10}D_8$ and $C_{10}H_8$ are partially reduced with potassium in THF and the THF is removed under reduced pressure, the reduced and unreduced naphthalenes can be separated into two phases.[8] Analysis of the anion radical phase and of the neutral phase reveals ratios of the two isotopic isomers that are in agreement with the solid-state free energy of electron transfer being very close to that found in solution.[8] Hence the −0.4 value in the third line of Table 2 is valid.

The quantitative quantum mechanical origin of equilibrium isotope effects, as shown in reaction 6, is complex, because the total change in ZPE stems from a number of opposing isotope effects on the various vibrations (e.g., eq 3).[3a] However, in a qualitative sense, the isotope effect upon hydrogenation is in the expected direction. The hydrogenation of naphthalene is destabilizing (loss of some aromaticity), and it is thermodynamically easier to destabilize the heavy isotopic isomer ($\Delta H° \approx$ −1800 cal/mol for reaction 6) than it is the light isotopic isomer.



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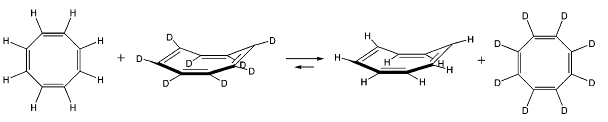

(7)

TABLE 2: Enthalpies of Reaction in kcal/mol

reaction	Δ*H*°	ref
$2K^+C_{10}H_8^{\bullet -}(s) + 2H_2O(liq) \rightarrow C_{10}H_{10}(s) + C_{10}H_8(s) + 2KOH(aq)$	−39.1	3, this work
$C_{10}D_8H_2(s) + C_{10}D_8(s) + 2KOH(aq) \rightarrow 2K^+C_{10}D_8^{\bullet -}(s) + 2H_2O(liq)$	+41.3	this work
$2K^+C_{10}D_8^{\bullet -}(s) + 2C_{10}H_8(s) \rightarrow 2K^+C_{10}H_8^{\bullet -}(s) + 2C_{10}D_8(s)$	−0.4	1, 5
$C_{10}D_8H_2(s) + C_{10}H_8(s) \rightarrow C_{10}D_8(s) + C_{10}H_{10}(s)$	+1.8 ± 0.5	

This is somewhat analogous to the ring flattening of cyclooctatetraene,[4] which is also destabilizing (gain of some antiaromaticity), and it is easier to destabilize the heavy isotopic isomer ($\Delta H° = -500$ cal/mol for reaction 7).

In general, the enthalpy for electron transfer from a perdeuteriated polyacene (A*) to the perprotiated polyacene ($A^{*\bullet -} + A \rightleftarrows A^{\bullet -} + A^*$) grows more exothermic as conjugation is extended,[7a] and enthalpies of hydrogenation and EAs increase as conjugation is extended. In fact, we have found a very linear empirical relationship between EA and the reciprocal of $\Delta H°_{H_2}$, having a slope of −481.2, Figure 5. Hence, it is anticipated that reaction 6 represents just a single example of many such isotope effects involving most of the polyaromatic hydrocarbons, including those shown in Figure 5, but the isotope effect upon $\Delta H°_{H_2}$ will be smaller for the larger polyacenes. The benzene system should yield a large isotope effect upon $\Delta H°_{H_2}$ and would be very interesting to study, but its solid anion radical is unstable toward dimerization.[9] The data for the perdeuteriated naphthalene system (red in Figure 5) correlate well with those for the perprotiated linear polyaromatics. This correlation allows the prediction of the heats of hydrogenation of the perdeuteriated linear polyaromatics.

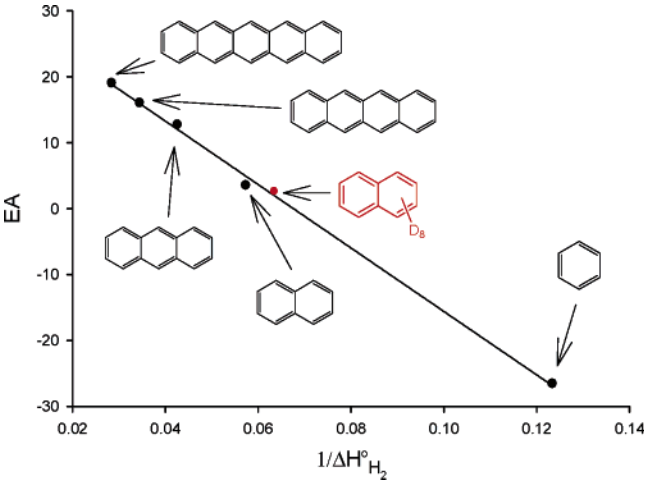

Figure 5. Plot of the EA in kcal/mol vs the reciprocal of the enthalpy of hydrogenation for the first five linear polyaromatic hydrocarbons. The EAs and $\Delta H°_{H_2}$'s were taken from Table 1 in ref 4a. The correlation coefficient for the line is 0.9991 (not including the point for $C_{10}D_8$). The intercept of 32.5 kcal/mol represents the predicted EA of an infinitely long linear polyacene. Long polyacenes are of extreme interest in terms of their electrical applications (see ref 10, wherein the synthesis of the largest known linear polyacene (heptacene) is described.

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