# Separation of Benzene and ^{2}H-Substituted Benzene via Potassium Reduction

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Perdeuteriated benzene can be partially separated from mixtures of perdeuteriated benzene and benzene simply by (1) reducing a mixture of C_6H_6 and C_6D_6 containing a molar deficient amount of 18-crown-6 (18C6) to the mixture with potassium metal and (2) distillation of the neutral benzenes from the metal–crown–anion radical complex, followed by (3) reoxidation of the anion radical back to the neutral benzenes. These isotopic enrichments are explained in terms of the less-than-unity equilibrium constant for the electron transfer [$K^+(18C6)C_6H_6^{\bullet-} + C_6D_6 = K^+(18C6)C_6D_6^{\bullet-} + C_6H_6$]. In this way the differences in the physical properties of an anion radical and a neutral molecule are utilized to separate isotopic mixtures. The differences in the chemical properties can also be used to effect similar separations. This was demonstrated by adding water to a partially reduced mixture of naphthalene and perdeuterionaphthalene. Since the solution electron affinity of the isotopically light material is larger than that of the perdeuteriated material, the water addition results in the formation of dihydronaphthalene and dihydroperdeuterionaphthalene with the ratio $[C_{10}H_{10}]/[C_{10}D_8H_2]$ being greater than the ratio $[C_{10}H_8]/[C_{10}D_8]$ in the original mixture.

It has been more than 15 years since Chang and Coombe[1] utilized ESR data to find that the partial reduction of a mixture of naphthalene ($C_{10}H_8$) and perdeuteriated naphthalene ($C_{10}D_8$) in tetrahydrofuran (THF) resulted in a ratio of anion radicals $[C_{10}H_8^{\bullet-}]/[C_{10}D_8^{\bullet-}]$ that is larger than the $[C_{10}H_8]/[C_{10}D_8]$ ratio used to make up the solution. That is, they observed preferential reduction of the isotopically light material. It is unfortunate that this report did not stimulate interest in the perturbation of solution reduction potentials due to deuteriation, since there exists the possibility of accomplishing isotopic enrichment from simple anion radical–neutral molecule separation. Perhaps, part of the reason for the lack of further work in this area was due to the following two facts: (1) it was not clear to all that line-width effects due to rapid electron transfer were accounted for in their ESR data and (2) their reported free-energy change of 600 cal/mol is not consistent with their equilibrium constant of 0.60 for reaction 1 at –60 °C.

$$C_{10}H_8^{\bullet-} + C_{10}D_8 \rightleftharpoons C_{10}H_8 + C_{10}D_8^{\bullet-} \qquad (1)$$
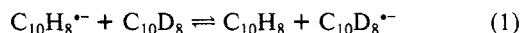
Much more recently, we[2a] have investigated the ESR pattern (with line-width effects rigorously accounted for)[2b,c] produced from the partial potassium reduction of a mixture of benzene and perdeuteriobenzene and found the equilibrium constant for reaction 2 to be 0.26 ± 0.10 at –120 °C in THF. The fact that the

$$C_6H_6^{\bullet-} + C_6D_6 \rightleftharpoons C_6H_6 + C_6D_6^{\bullet-} \qquad (2)$$
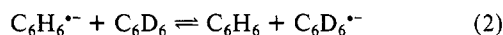
equilibrium constant is well below unity implies that a physical separation of the anion radicals from the neutral molecules would effect a partial but significant separation of the two isotopic isomers.

Results and Discussion

When 4 g of a mixture of C_6H_6 and C_6D_6 ($[C_6H_6]/[C_6D_6]$ = 1.1) containing 0.428 mmol of 18-crown-6 (18C6) is exposed to a freshly distilled potassium mirror under high vacuum, the anion radicals are generated as previously described.[3] The anion radical salt exists in the presence of the large molar excess of neutral benzenes, and the following equilibrium is established:[4]

$$(3)$$

(1) Chang, R.; Coombe, R. *J. Phys. Chem.* **1971**, *75*, 447.
(2) (a) Stevenson, G. R.; Espe, M. P.; Reiter, R. C. *J. Am. Chem. Soc.* **1986**, *108*, 532. (b) Stevenson, G. R.; Lovett, D. J.; Reiter, R. C. *J. Phys. Chem.* **1986**, *90*, 4461. (c) Stevenson, G. R.; Alegria, A. E. *J. Phys. Chem.* **1976**, *80*, 69.
(3) (a) Weissman and Komarynsky[3b] found the manner in which the anion radicals of benzene and alkyl-substituted benzenes are formed by exposing a dilute solution of a crown ether dissolved in the respective aromatic hydrocarbon to alkali metal in the absence of any other solvent. (b) Weissman, S. I.; Komarynsky, M. A. *J. Am. Chem. Soc.* **1975**, *97*, 1589.

TABLE I: Molar Ratio of Benzene to Perdeuteriated Benzene in both Phase 1 (Neutral Benzenes) and Phase 2 (Anion Radical), Millimoles of 18-Crown-6, and Isotope Separation Factor

18C6, mmol	$([C_6H_6]/[C_6D_6])_1$	$([C_6H_6]/[C_6D_6])_2$	α
0.480	0.266 ± 0.008	0.485 ± 0.019	1.8
0.449	0.694 ± 0.015	1.083 ± 0.053	1.6
0.428	1.100 ± 0.056	1.819 ± 0.014	1.7

Separation of the liquid mixture from the metal followed by distillation of the neutral benzenes (collected as phase 1) under reduced pressure leaves the solid (dark red) $K(18C6)^+$, anion radical salt (phase 2). This anion radical salt was left exposed to high vacuum (10^{-6} Torr) to ensure complete removal of the neutral benzenes and eliminate the possibility of isotope separation due to the difference in the vapor pressures of C_6D_6 and C_6H_6.[5] Phase 1 has the same isotopic ratio as does the initial mixture, as only a very small fraction of the benzenes is reduced to the anion radical. The addition of I_2 dissolved in ether to phase 2 results in the reoxidation of the anion radicals back to the neutral benzenes, reaction 4.

$$2K(18C6)^+C_6H_6^{\bullet-} + I_2 \rightarrow 2K(18C6)^+I^- + 2C_6H_6 \qquad (4)$$
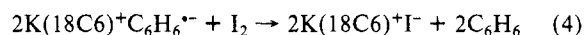
Mass spectral analysis shows that when the separations described above were carried out at room temperature, the molar ratio of $[C_6H_6]/[C_6D_6]$ had changed from the original value of 1.1 to 1.82, which represents a separation factor of α = $([C_6H_6]/[C_6D_6])_2/([C_6H_6]/[C_6D_6])_1$ of 1.7. Several such experiments show that the partial separation is so great that it should be readily observable in the ^{13}C NMR spectra of the two phases. The reduction of larger fractions (25%) of the benzene isotopic mixture, where 7.5 mmol of 18C6 is present and the original molar ratio of $[C_6H_6]/[C_6D_6]$ is about 1/4, followed by the same separation procedure, was carried out. As predicted, the ^{13}C NMR spectra of the two samples do indicate an enrichment of C_6H_6 in phase 2 and an enrichment of C_6D_6 in phase 1 (Figure 1). Integration of the NMR spectra yields a separation factor of 1.6 ± 0.2, which is in quantitative agreement with the value of 1.7 obtained from the mass spectral results.

The separation factor of 1.7 ± 0.1 (Table I) corresponds to an equilibrium constant of 0.59 ± 0.04 for reaction 3. The free energy change, which is identical with the enthalpy change, for reaction 2 is 410 ± 12 cal/mol.[2] This corresponds to an equilibrium constant of K_{eq} = exp(−410/RT) = 0.50 ± 0.02 at room temperature. The separation factor and previously reported equi-

(4) The rate of electron transfer from anion radical to neutral molecule is very fast ($(1–2) \times 10^5$ M^{-1} s^{-1}) in an absolute sense, but it is slow compared to other such electron-transfer reactions due to the close association between the encapsulated cation and the anion radical.[3b]
(5) Jancso, G.; Van Hook, W. A. *Chem. Rev.* **1974**, *74*, 689.
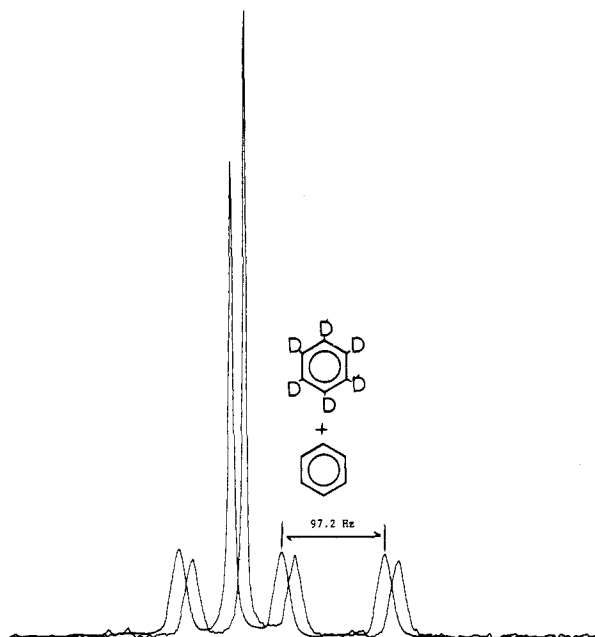
Figure 1. Shifted to the left is the proton decoupled ^{13}C NMR spectrum of a mixture of C_6H_6 and C_6D_6 consisting of $[C_6H_6]/[C_6D_6] = 0.25$. Shifted to the right is the ^{13}C NMR spectrum of material taken from this same mixture after reduction with potassium in the presence of 18C6, removal of the unreduced benzenes, and reoxidation of the anion radicals. Note that the triplet for C_6D_6 in the spectrum offset to the right is larger than that for the spectrum offset to the left. However, the signal for C_6H_6 is smaller in the spectrum on the left (the $[C_6H_6]/[C_6D_6]$ ratio is larger in the spectrum shifted to the left). Both spectra were recorded under identical conditions (1000 scans, 10-s pulse delay, 14-μs pulse width, same decoupling and lock signal power, etc.) in deuteriated chloroform. The separation factors were not obtained from these NMR spectra but from mass spectral analysis. However, these spectra obviate any doubt as to the reality of the isotopic separation.

librium constant are in rather good agreement, especially considering the fact that the solvent systems are very different.

This separation of anion and neutral molecule by physical means (distillation) is certainly the most efficient means for isotope enrichment involving reactions 1 or 2. However, separation via chemical reaction of the anion radical is also possible. If the equilibrium constant for reaction 1 is indeed below unity as claimed by Chang and Coombe[1] and us,[2] then the addition of water to the reaction mixture produced by the partial reduction of a 1:1 mixture of $C_{10}H_8$ and $C_{10}D_8$ should afford more dihydronaphthalene ($C_{10}H_{10}$) than deuteriated dihydronaphthalene ($C_{10}D_8H_2$).

A 1:4 molar mixture of $C_{10}H_8$ and $C_{10}D_8$ was divided into two portions. One portion was completely reduced with excess potassium metal, and the other was reduced with only half the stoichiometric amount of metal in THF. Both reactions were then quenched with an excess of water, yielding the Birch reduction products, reaction 5.
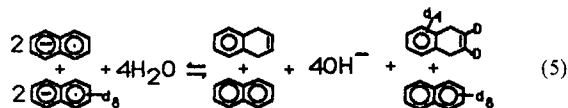
The proton decoupled ^{13}C NMR analysis of the vinyl carbons shows that the triplet (C–D vinyl carbon) is more intense relative to the singlet (C–H vinyl carbon) in the partially reduced mixture than it is in the fully reduced mixture (Figure 2). Integration of the NMR lines shows that the triplet due to the C_2D_2 vinyl fragment is 2.30 times larger than that for the NMR line due to the C_2H_2 fragment when the spectrum is recorded from a sample that results from the addition of water to a partially reduced ($^1/_2$ mol of metal per mole of naphthalenes) mixture of $C_{10}H_8$ and $C_{10}D_8$. However, when the NMR sample comes from a fully reduced mixture, the triplet intensity is only 0.95 times as large as the intensity of the C_2H_2 signal.
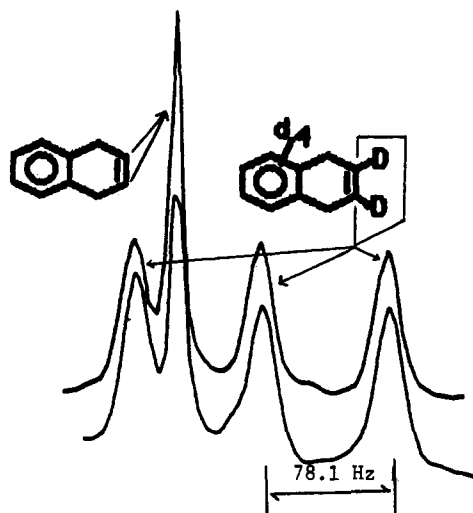
Figure 2. (Lower) NMR spectrum of the vinyl carbon of the dihydronaphthalenes obtained from the addition of an excess of water to a fully reduced (1 mol of K per mole of naphthalene) mixture of $C_{10}H_8$ and $C_{10}D_8$ ($[C_{10}H_8]/[C_{10}D_8] = 1/4$). (Upper) NMR spectrum of the products obtained from the addition of water to a partially reduced (0.5 mol of K per mole of naphthalene) sample of this same mixture. Note that although the spectral intensity for the deuteriated carbon is about the same in both spectra, the signal for the protiated carbon is larger in the upper spectrum. The spectra were recorded in deuteriated chloroform under identical conditions.
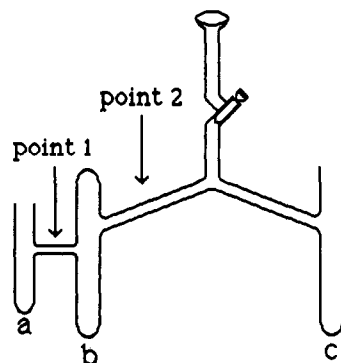
Figure 3. Apparatus used for the anion radical generation and isotopic isomer separation.

If the addition of the water results in the trapping of both anion radicals in the concentrations that existed in the equilibrium mixture, then 0.95/2.30 should represent the equilibrium constant of reaction 1. This value of 0.41 ± 0.04 is in agreement with that predicted (assuming $\Delta H^\circ = \Delta G^\circ = 412$ cal/mol) for reaction 1. The equilibrium constant of 0.26 at $-120\ ^\circ$C[2] corresponds to an equilibrium constant of 0.49 ± 0.03 at room temperature.

Although there are a number of kinetic arguments involving the mechanism of the Birch reduction that could account for the preferential formation of the hydrogenated isotopically light isomer, a simple equilibrium isotope effect ($K_{eq} < 1$ for reaction 1) is the simplest. Further, only this simple equilibrium isotope effect can account for the separation of the deuteriated benzene from benzene using the crown ethers.

Experimental Section

Benzene Experiments. Bulb c of the apparatus shown in Figure 3 was charged with 0.1 to 0.6 mmol of 18C6 and sealed. A molar excess of potassium metal was placed into bulb a, which was subsequently sealed. The apparatus was then connected to the vacuum line and evacuated. The system was left exposed to the vacuum (10^{-3} Torr) for several hours to remove any moisture in the 18C6. The potassium was then distilled into bulb b, and bulb a was subsequently sealed from the apparatus at point 1. Aliquots of 20–100 mmol of benzene–perdeuteriated benzene mixtures were then distilled into bulb c from the potassium metal through the vacuum system. The apparatus was then removed from the

vacuum system and tilted to allow exposure of the benzenes–18C6 mixture to the potassium mirror. After dissolution of a mole of potassium metal for each mole of 18C6, the bulb containing the excess potassium (bulb b) was sealed from the apparatus at point 2, and the apparatus was reconnected to the vacuum system. All of the unreduced benzenes were then distilled under vacuum into a container on the vacuum line and saved as phase 1 for mass spectral and NMR analysis. The remaining potassium–crown–benzene complex was then left exposed to high vacuum (10^{-6} Torr) to ensure complete removal of the unreduced benzenes.

About 5 mL of diethyl ether containing a molar excess of iodine was then distilled and sublimed directly onto the potassium–crown ether–benzene complex. The resulting reaction reoxidizes and liberates the benzenes, reaction 4. These reoxidized benzenes (phase 2) were then distilled and submitted to mass spectral and NMR analysis. In all experiments phase 2 proved to be highly enriched in the light isotopic isomer as compared to phase 1.

Naphthalene Experiments. Mixtures of naphthalene and perdeuteriated naphthalene (1:4) were prepared by dissolving carefully weighed portions of each in diethyl ether. The ether solution was then divided into two portions, and the ether was allowed to evaporate under a nitrogen atmosphere. Both portions were reduced in THF on a potassium metal mirror in the apparatus shown in Figure 3. However, for one portion, bulb b was charged

with only half of the stoichiometric amount of metal needed for complete reduction, and the other portion was completely reduced with an excess of metal. Water was then added to both reactions through the stopcock.

The resulting organic materials were extracted with ether. The ether was dried with sodium sulfate and removed via evaporation. The naphthalene–dihydronaphthalene mixtures were then sublimed and dissolved in deuteriated chloroform for NMR analysis. Integration of the proton decoupled NMR spectra shows that each component of the C–D vinyl carbon triplet is more intense than the C–H vinyl carbon singlet by a factor of 1.2 for the completely reduced sample. However, this ratio is only 0.80 for the partially reduced sample. This corresponds to a separation factor of 1.5.

All ^{13}C NMR spectra were recorded in 10-mm tubes on a Joel FX 90Q NMR spectrometer. Mass spectral analysis was carried out on a Hewlett-Packard 5790 GC mass spectrometer with 30-m, 0.25 mm i.d. capillary columns of methylphenyl silicone. The isotopic ratios were determined from eight independent measurements of the 84/78 peak intensities.

COMMENTS

Photocatalytic Reactor Design: An Example of Mass-Transfer Limitations with an Immobilized Catalyst

Sir: In a recent article,[1] a novel coiled glass-tube reactor was used to examine heterogeneous photocatalytic degradation kinetics. Earlier studies of kinetics of heterogeneously photocatalyzed systems[2-5] have characteristically used slurries of fine catalyst particles of, e.g., 0.1 wt % catalyst. For 0.2- and 0.03-μm particles, as typify earlier Fisher Chemical and Degussa TiO_2 sources, in 0.001 weight fraction of solids (density 3.9 g/mL), the maximum reactant diffusion distance to the catalytic solid is half the mean particle spacing, or 3 and 0.5 μm, respectively. For the coiled tube reactor of 2-mm radius, the corresponding maximum transport distance is the centerline-to-catalyst coated wall distance of 2000 μm (2 mm). Thus, this reactor configuration, as well as a catalyst-coated packed bead column,[6] clearly increases the average distance which a dissolved reactant must diffuse in order to reach the photocatalytically active surface. One must consider that the dependence of reactant removal rate on solution-to-catalyst diffusion/convection mass transfer, found to be negligible for 0.1 wt % catalyst slurry systems,[7] may be significant for thin films of fixed catalyst. If so, the mass-transfer influence must be recognized and included in a proper kinetic analysis, as is traditionally done.[8,9]

We will calculate mass-transfer rates based entirely on geometry and fluid properties to show that the results reported by Matthews were completely or largely dependent on reactant convective diffusion to the tube wall rather than inherent surface reaction kinetics. Carbonell made similar use of mass-transfer relations to show a mass-transfer influence on enzyme kinetics in a coiled tube.[10] The TiO_2 deposited film thickness was approximately 0.2 μm, roughly an order of magnitude less than that required for opacity,[11] and therefore a nearly constant illumination intensity was expected on the tube wall. We proceed by calculating mass-transfer coefficients (or equivalently mass-transfer Nusselt numbers, Nu) for both the straight tube and coiled tube cases. Rates of removal based on the mass flux from the moving fluid to the interior tube surface will be compared to Matthews' experimental results.

Matthews examined the degradation of several aromatic compounds and reported an increase in rate of reactant disappearance with increasing flow rate, a strong clue of diffusionally influenced kinetics. For salicylic acid, he reported a series of reaction rates for flowrates from 30 to 420 mL/min. These flows represented Reynolds numbers from 180 to 2500; thus the reactor was in the laminar flow regime everywhere. (The upper values appear to be within the transition region from laminar to turbulent flow, usually taken to begin at Re = 2100 for smooth straight tubes. However, fluid flow through coiled tubes is stabilized so that the laminar flow region is extended to higher Re.[12])

Most of the correlations for transfer in coiled tubes were developed for heat transfer.[13] However, the established similarity of the heat- and mass-transfer mechanisms make the relations

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