

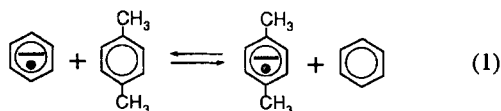
SOLUTION ELECTRON AFFINITY CHANGES VIA THE DEUTERIATION OF THE METHYL GROUPS OF *p*-XYLENE

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EPR techniques, including spectral double integration, were utilized to measure the equilibrium constants in dimethoxyethane at 195 K for electron transfer between perdeuteriated *p*-xylene and xylene, α -*d*₃-*p*-xylene and α , α' -*d*₆-*p*-xylene. The results, coupled with the law of Hess, yield all the relative solution electron affinities (EA). It was found that methyl deuteration lowers the solution EA by 160 J mol⁻¹ per deuterium, whereas ring deuteration in these systems lowers the solution EA by about 370 J mol⁻¹ per deuterium, which is about the same effect as is observed in the benzene system. The results are discussed in terms of hyperconjugative, inductive and solvation effects.

INTRODUCTION

It has been known for over 100 years that electrophilic attack of methyl-substituted benzenes in solution is controlled by the ring-activating and *ortho*-*para*-directing nature of this substituent.¹ This effect is currently understood in terms of the net electron-donating nature of the methyl group, which is the net result of three factors: electron-releasing inductive interactions, hyperconjugative interactions and steric inhibition to ion-solvent interactions. The net electron-donating nature of the methyl substituent is perhaps most simply demonstrated by the decreased solution electron affinity (EA) of methyl substituted benzenes relative to benzene.² When mixtures of *p*-xylene and benzene were partially reduced with alkali metal in a solvent mixture of dimethoxyethane (DME) and tetrahydrofuran (THF), the EPR analysis of the resulting relative anion radical concentrations proved reaction (1) to have a positive ΔG° . It was suggested that the endothermic ($\Delta G^\circ = \Delta H^\circ$, $\Delta S^\circ = 0$) nature of this reaction should persist into the gas phase.²



$$\Delta G^\circ = +3200 \text{ J mol}^{-1} \text{ in solution}$$

$$\Delta G^\circ = -7700 \text{ J mol}^{-1} \text{ in gas phase}$$

This prediction did not hold up, however, and the exothermicity of the electron transfer was demonstrated in the gas phase,³ which can only mean that steric

inhibitions to ion-solvent interactions play an important role in controlling the solution-phase electron transfer. Without the presence of the solvent and counter ion, the methyl groups are intrinsically electron attracting in nature. Thus, the hyperconjugative effect is dominant in the gas phase. That is, the gas-phase equilibrium is biased in favor of the molecule with the most delocalization, and the two methyl groups allow the negative charge to be delocalized into six additional atomic centers.

The solution-phase EPR spectra of the anion radical of both *p*-xylene (CH₃C₆H₄CH₃) and α , α' -*d*₆-*p*-xylene (CD₃C₆H₄CD₃) reveal a splitting associated with the lifting of the degeneracy of the two antibonding MOs into which the extra electron is added. However, to a first-order approximation the presence of two methyl groups should not cause a deviation of the gas-phase free energy change for reaction (1) from zero (Figure 1, top). The simple HMO model predicts that the two CH₃ groups do increase the energy of the symmetric orbital given by $\Psi_s = 1/\sqrt{12}(2\Psi_1 - \Psi_2 - \Psi_3 + 2\Psi_4 - \Psi_5 - \Psi_6)$, but the electron would be expected to add into the antisymmetric orbital given by $\Psi_a = (1/2)(\Psi_2 - \Psi_3 + \Psi_5 - \Psi_6)$, which is not perturbed by the CH₃ groups. This ordering of the two MOs is confirmed by solution-phase EPR studies,⁴ but it is unclear if this ordering persists in the gas phase.³

EPR studies show that the anion radicals of α -*d*₃-*p*-xylene (CD₃C₆H₄CH₃⁻) and α , α' -*d*₆-*p*-xylene (CD₃C₆H₄CD₃⁻) exhibit hyperfine coupling constants for the ring protons that are 12 and 23 mG larger than those of the *p*-xylene anion radical itself.⁵ This has been attributed to a further lifting of the degeneracy of

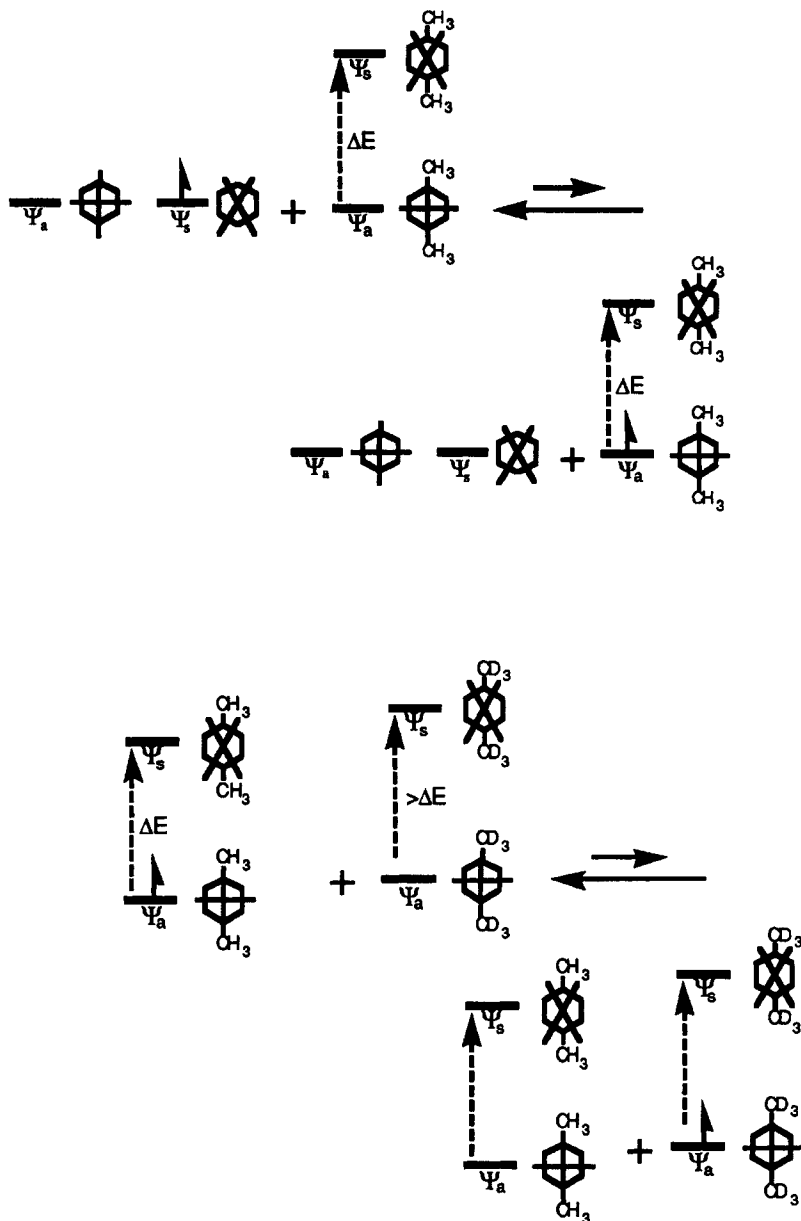
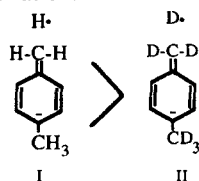


Figure 1. Top: The electron transfer reaction between benzene and *p*-xylene showing the molecular orbitals into which the extra electron is being added. The methyl groups are shown splitting the degeneracy (raising) of the two antibonding MOs, but this cannot account for the endothermic nature of this reaction in solution. A second order effect (which is not shown) resulting in the lifting of Ψ_a must also result from the presence of the methyl groups. Bottom: The electron transfer reaction between *p*-xylene and α, α' - d_6 -*p*-xylene showing the molecular orbitals into which the extra electron is being added. The inductive lifting of the antisymmetric orbital by the two deuteriated methyl groups accounts for the endothermic nature of this reaction

the antibonding molecular orbitals due to the replacement of the protons with deuteriums to an extent of about 29 J mol^{-1} per deuterium. These results seem to support the conclusion that the hyperconjugative effect is a result of the interaction between the methyl antibonding orbital and the ring, and it lowers the energy of Ψ_s in xylene and toluene.⁶ Thus, hyperconjugation itself seems to stabilize Ψ_s relative to Ψ_a , and consideration of the inductive effect, which is augmented by deuteration, is necessary for the proper ordering of Ψ_s and Ψ_a . It should be noted that manifestations of deuterium perturbations upon hyperconjugation have also been noted via NMR studies.⁷

Within the confines of the Born–Oppenheimer approximation, methyl group deuteration should lower the magnitude of the hyperconjugative effect. This is the case since methyl group deuteration lowers the zero point energies of the methyl C—H bonds and, in turn, attenuates contributions from the methyl–ring interaction (valence bond structure I contributes to a greater degree than does structure II). This diminishes the hyperconjugative effect of lowering of Ψ_s relative to Ψ_a and leads to an increase in the relative contribution from the inductive effect, hence the observed isotopic increase in the splitting of the two antibonding MOs (ΔE) due to deuteration.



What would be the effect upon the solution electron affinity of replacing the methyl protons with deuteriums? The replacement of the *para*-hydrogens in benzene with CH_3 groups amplifies the EPR observed splitting and simultaneously reduces the solution electron affinity. The replacement of the CH_3 groups with CD_3 groups further amplifies the EPR observed splitting. Thus, by analogy, we might expect a simultaneous decrease in the solution *EA*. However, it is a solvation effect (steric inhibition to solvation) that renders the solution *EA* of xylene less than that of benzene. A change in solvation should take place upon replacement of the methyl groups with CD_3 groups in the xylene anion radical because the C—D bond is shorter than the C—H bond [for naphthalene, *x*-ray crystallography reveals a reduction of the C—L (L = H or D) bond length from 1.085 (C—H) to 1.073 (C—D) Å⁸], and slightly less steric inhibition to solvation from the CD_3 s is expected. From this (solvation effect) point of view, the solution *EA* of the α -deuterated xylenes should be just very slightly larger than that of xylene. In support of this prediction, it has been observed that the very small changes in steric requirements due to D for H substitution can lead to

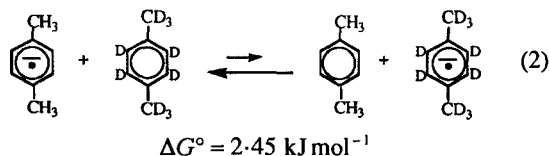
large alterations in macroscopic physical properties.⁹ On the other hand, the general bond weakening that takes place upon electron attachment should be more extensive in the deuterated compound and render its *EA* lower than that of the perprotiated compound. It is this general bond weakening that renders the solution *EA* of perdeuterated benzene less than that of benzene.^{10,11}

RESULTS

The EPR technique could not be used to directly compare the solution *EAs* of $\text{CD}_3\text{C}_6\text{H}_4\text{CD}_3$, $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_3$, and $\text{CD}_3\text{C}_6\text{H}_4\text{CH}_3$ because the EPR spectra of each of the resulting pairs of anion radicals are too similar. Rather, the competitive electron transfer equilibria of those species with $\text{CD}_3\text{C}_6\text{D}_4\text{CD}_3$ were studied.

When a solution of 100 mg of perdeuterated *p*-xylene ($\text{CD}_3\text{C}_6\text{D}_4\text{CD}_3$) in approximately 4 ml of dimethoxyethane (DME) and a very deficient molar amount of 18-crown-6 is exposed to a freshly distilled potassium metal mirror under high vacuum at -78°C , a solution of the anion radical of $\text{CD}_3\text{C}_6\text{D}_4\text{CD}_3$ is formed. Dilution of this sample with more DME yields a solution whose EPR analysis at 195 K indicates that the anion radical exists in two different states of ion association, both with observable metal hyperfine splittings. The ratio of concentrations of the two ion pairs is 1 : 1, and $a_K = 0.0725$ and 0.142 G , respectively. These metal splittings were expected and are just slightly larger than those reported for the *p*-xylene anion radical under identical conditions.⁵

The reduction of 22.3 mg (0.21 mmol) of *p*-xylene and 152.0 mg (1.31 mmol) of perdeuterated *p*-xylene in approximately 4 ml of DME containing a deficient molar amount of 18-crown-6 by a very molar deficient amount of potassium metal yields a solution of the anion radicals of *p*-xylene and perdeuterated *p*-xylene. The EPR spectrum of the anion radicals is best simulated by assuming an anion radical mixture corresponding to $[\text{CD}_3\text{C}_6\text{D}_4\text{CD}_3^-]/[\text{CH}_3\text{C}_6\text{H}_4\text{CH}_3^-] = 1.33$ (Figure 2). Thus, the equilibrium constant for reaction (2) that best fits this experiment is $1.33 \times (0.21/1.31) = 0.21$. Several such experiments reveal that K_{eq} for reaction (2) is 0.22 ± 0.02 at 195 K.



Similar experiments were carried out using mixtures of $\text{CD}_3\text{C}_6\text{D}_4\text{CD}_3$ with $\text{CD}_3\text{C}_6\text{H}_4\text{CH}_3$ and with $\text{CD}_3\text{C}_6\text{H}_4\text{CD}_3$. The law of Hess was utilized to obtain the equilibrium constants for the electron transfer reactions for the systems not containing $\text{CD}_3\text{C}_6\text{D}_4\text{CD}_3$ (Table 1).

Table 1. Equilibrium constants and free energy changes in J mol^{-1} for the electron transfer from the anion radical (columns) to the neutral molecule (rows) at 195 K in DME

	$\text{CH}_3\text{C}_6\text{H}_4\text{CH}_3$	$\text{CD}_3\text{C}_6\text{H}_4\text{CH}_3$	$\text{CD}_3\text{C}_6\text{H}_4\text{CD}_3$	$\text{CD}_3\text{C}_6\text{D}_4\text{CD}_3$
$\text{CH}_3\text{C}_6\text{H}_4\text{CH}_3^-$	1.00	0.79 ± 0.11	0.55 ± 0.07	0.22 ± 0.02
	0.00	390 ± 230	970 ± 220	2450 ± 150
$\text{CD}_3\text{C}_6\text{H}_4\text{CH}_3^-$	1.27^a	1.00	0.70 ± 0.10	0.28 ± 0.03
	-390	0.00	580 ± 230	2060 ± 170
$\text{CD}_3\text{C}_6\text{H}_4\text{CD}_3^-$	1.8	1.43^a	1.00	0.40 ± 0.04
	-970	-580	0.00	1480 ± 160
$\text{CD}_3\text{C}_6\text{D}_4\text{CD}_3^-$	4.5	3.6	2.5	1.00
	-2450	-2060	-1480	0.00

^a A third significant figure was retained in these K_{eq} values in order that calculated ΔG° values for the forward and reverse reactions agree appropriately.

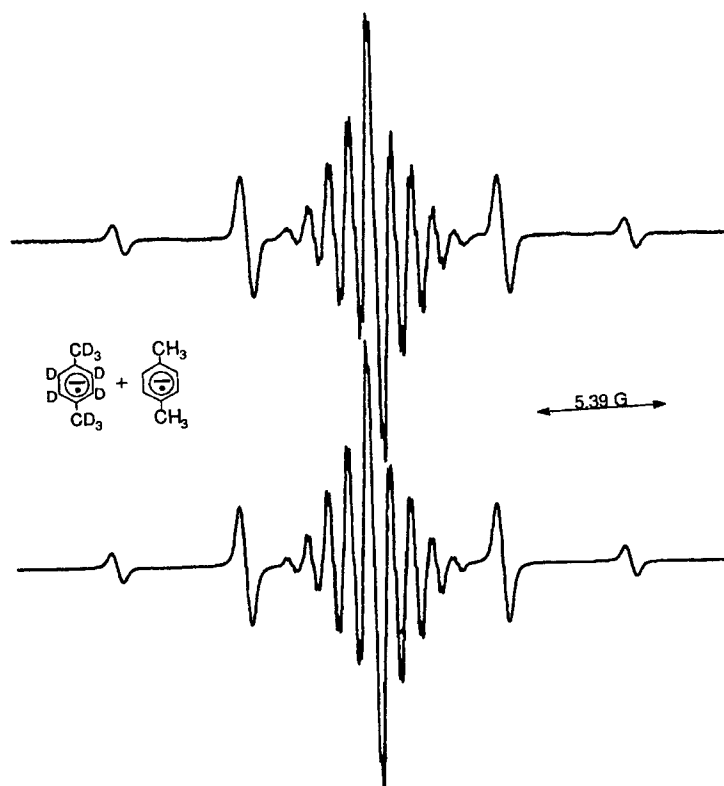


Figure 2. EPR spectrum at 195 K resulting from the partial (about 5%) potassium reduction of a mixture of *p*-xylene and perdeuteriated *p*-xylene ($[\text{CH}_3\text{C}_6\text{H}_4\text{CH}_3]/[\text{CD}_3\text{C}_6\text{D}_4\text{CD}_3] = 0.160$) in DME containing 18-crown-6. The computer simulation (bottom) was generated using a ratio of anion radicals $[\text{CH}_3\text{C}_6\text{H}_4\text{CH}_3^-]/[\text{CD}_3\text{C}_6\text{D}_4\text{CD}_3^-] = 0.75$. The ring and methyl proton splittings used in the simulation are 5.386 and 0.100 G, respectively. For the analogous deuteriums, the a_{D} s are 0.865 and 0.013 G.

Four of the five widely spaced packets of hyperfine components from the ring-protiated xylene anion radicals lie outside of the field covered by the spectrum of $\text{CD}_3\text{C}_6\text{D}_4\text{CD}_3^-$. This situation provides us with the opportunity to utilize double integration of the spectra to

obtain K_{eq} . The extremities of the doubly integrated spectrum account for 10/16ths of the ring protiated anion radical concentration, while the central portion accounts for 6/16ths of this concentration and all of the $\text{CD}_3\text{C}_6\text{D}_4\text{CD}_3^-$ concentration. The double integration technique

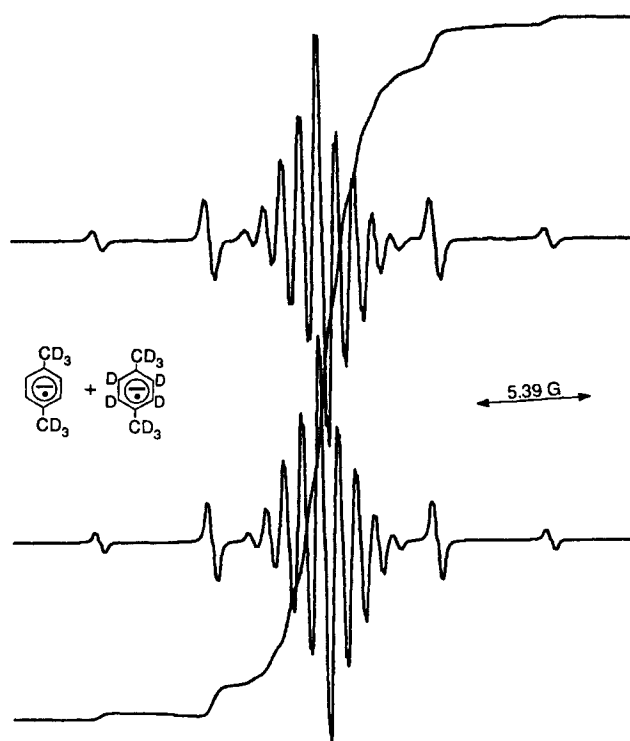


Figure 3. EPR spectrum at 195 K resulting from the partial (about 5%) potassium reduction of a mixture of α,α' -*d*₆-*p*-xylene and perdeuterated *p*-xylene ($[\text{CD}_3\text{C}_6\text{H}_4\text{CD}_3]/[\text{CD}_3\text{C}_6\text{D}_4\text{CD}_3]=0.112$) in DME containing 18-crown-6. The computer simulation (bottom) was generated using a ratio of anion radicals $[\text{CD}_3\text{C}_6\text{H}_4\text{CD}_3^-]/[\text{CD}_3\text{C}_6\text{D}_4\text{CD}_3^-]=0.270$. These results yield an equilibrium constant of 0.41 for the electron transfer: $\text{CD}_3\text{C}_6\text{H}_4\text{CD}_3^- + \text{CD}_3\text{C}_6\text{D}_4\text{CD}_3 = \text{CD}_3\text{C}_6\text{H}_4\text{CD}_3 + \text{CD}_3\text{C}_6\text{D}_4\text{CD}_3^-$. The double integration of the real spectrum (shown superimposed) allows unambiguous accounting for the outer four lines or 10/16ths of the $\text{CD}_3\text{C}_6\text{H}_4\text{CD}_3^-$ concentration. The central up slope of the double integration accounts for all of the $\text{CD}_3\text{C}_6\text{D}_4\text{CD}_3^-$ concentration and the central component or 6/16ths of the light anion radical concentration. The ratio of anion radical concentrations obtained from this double integration is $[\text{CD}_3\text{C}_6\text{H}_4\text{CD}_3^-]/[\text{CD}_3\text{C}_6\text{D}_4\text{CD}_3^-]=0.252$

(Figure 3) yields equilibrium constants similar to those obtained from the use of computer simulations.

CONCLUSIONS

The replacement of the methyl hydrogens with deuteriums has the same qualitative effect upon the solution *EA* as does the substitution of the ring protons: it lowers the solution *EA*. This is consistent with an increased electron-donating inductive effect upon CH_3 replacement with CD_3 and a reduction of the hyperconjugative effect. The quantitative effect of deuteration of the methyl groups upon solution *EA* amounts to about 160 J mol^{-1} per deuterium, while that for deuteration of the ring positions in *p*-xylene is about 370 J mol^{-1} per deuterium. This latter value is very close to the value reported for the replacement of ring hydrogens with deuteriums in benzene (380 J mol^{-1} per deuterium).¹¹

The slightly diminished steric inhibition to solvation that would be expected upon replacement of the methyl groups with CD_3 s is overwhelmed by the intramolecular inductive and hyperconjugative contributions to the solution *EA*. Based upon the previously observed increase in the ring proton coupling constant, this isotopic substitution diminishes the hyperconjugative effect of lowering Ψ_3 , leading to an increase in ΔE .⁵ In order to account for the simultaneous decrease in solution *EA*, the presence of the methyl deuteriums must also inductively raise the energy of the molecular orbital to which the electron is added (Ψ_4 in Figure 1, bottom).

EXPERIMENTAL

In a typical electron competition experiment, 15 mg of *p*-xylene and 149.1 mg of *d*₁₀-*p*-xylene were sealed in a

capillary tube and placed in an apparatus along with one tenth the molar equivalent of 18-crown-6. Approximately 4 ml of DME were distilled from an evacuated bulb containing NaK₂ into the evacuated apparatus, which was then sealed from the vacuum line and agitated so as to break the capillary tube. The resulting solution was then briefly exposed to a freshly distilled potassium mirror and the resulting anion radical solution poured into an attached 4 mm tube.

All the EPR spectra were recorded with a Bruker ER-200 EPR spectrometer equipped with an IBM variable-temperature unit connected to the back cavity of a dual-cavity system at 195 K. The spectra were saved on disk with EPRWare data collection software.^{12a} Simulations were carried out using the software described previously.^{12b,c}

α,α' -*d*₆-*p*-Xylene and *d*₁₀-*p*-xylene were purchased from MSD Isotopes. α -*d*₃-*p*-Xylene was not commercially available and was synthesized using a variation of the procedure reported for *p*-xylene.¹³

A 40 ml volume of dry light petroleum (b.p. 30–60 °C) and 3.44 g of cut sodium spheres were placed in a 100 ml three-necked round-bottomed flask under a stream of nitrogen. *p*-Chlorotoluene (9.50 g) was introduced from a dropping funnel with vigorous stirring. Stirring continued at 30 °C for 3 hours, after which 9.81 g of perdeuterated dimethyl sulfate in 3.75 ml of freshly distilled benzene were introduced over the span of 1 hour with the temperature maintained at 30 °C. Water was then slowly added to the colorless reaction mixture, and the organic layer was separated. The lighter materials were distilled from the organic mixture at 90 °C. The remaining crude xylene was then steam distilled in the presence of 0.1 M potassium hydroxide. The organic layer was separated from the distillate and dried over magnesium sulfate. This mixture was distilled, and the α -*d*₃-*p*-xylene was collected at 137–138 °C. This α -*d*₃-*p*-xylene was further purified via preparative gas chromatography.

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