Benzene Radical Ion in Equilibrium with Solvated Electrons

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Radical anions of benzene (C_6H_6) and its monofluoro and -methyl derivatives are found to exist in equilibrium with solvated electrons in THF solution. At 298 K $C_6H_6^{\bullet-}$ is less stable than the solvated electron with K_{eq}= 0.22 M^{-1}, but at lower temperatures $C_6H_6^{\bullet-}$ is favored, K_{eq} reaching 65 M^{-1} at 218 K. The energetics ($\Delta H°$ = −26 kJ/mol; $\Delta S°$ = −101 J/deg mol) are remarkable because the same reaction is endoergic by 1.17 eV in the gas phase. For fluorobenzene, K_{eq} =1.7 × 10^2 M^{-1} at 298 K and is also strongly temperature-dependent with a similar, large negative entropy change ($\Delta H°$ = −49 kJ/mol; $\Delta S°$ = −121 J/deg mol). The energetics can be understood by taking into account a substantial (∼1 eV) electronic energy of the solvated electron. The large apparent "entropy changes" may include changes that are not entropic, but arise instead from temperature and density dependent enthalpy changes. The optical absorption spectrum of $C_6H_6^{\bullet-}$ is similar to that reported at 77 K. As would be expected for an ion of small size, $C_6H_6^{\bullet-}$ forms strongly bound ion pairs with Na$^+$; the dissociation constant for ($C_6H_6^{\bullet-}$,Na$^+$) ion pairs is 4.5 × 10^{-10} M. This strong ion pairing stabilizes $C_6H_6^{\bullet-}$ when a counterion is available, explaining why the ion-pair, but not the free ion of benzene, is readily observed.

Introduction

Benzene radical anion is known in cryogenic media,[1−4] at high pressures,[5] or as a cluster anion with water in a supersonic jet.[6] As an ion-pair it has been observed in solution at low temperatures, and even near room temperature.[7,8] Both benzene and toluene anions have been crystallized as K$^+$/crown ether salts and their structures obtained.[9] However, the free radical ion is not known in solution at normal temperature and pressure; the rare reports[10] of its existence are unconfirmed or discounted:[11] And why should it exist given that the electron affinity of benzene is −1.17 eV in the gas phase [12,13] and in ammonia $C_6H_6^{\bullet-}$ has been reported[14] to be far less stable than the solvated electron? Under ambient conditions energetics and even the existence of the $C_6H_6^{\bullet-}$ are not known, but estimates of the reduction potential for benzene have been obtained.

In carefully purified fluid ethers and alkylamines at low-temperature $C_6H_6^{\bullet-}$ was produced electrochemically. The appearance potential for the EPR spectrum provided estimates of −3.31 V vs SCE for the reduction potential of benzene[15,16] and other compounds, although the value[16] for paracyclophane appeared incorrect. Heinze and co-workers[17] used cyclic voltametry to observe part of the reduction wave and simulation to extract the reduction potential −3.35 V vs Ag/AgCl from a background of solvent decomposition. At −90 °C Kukharenko and Strelets reported a reversible potential for reduction of benzene[18] at −3.38 V vs SCE in electrochemical experiments in THF that probably produced $C_6H_6^{\bullet-}$ stabilized by ion pairing.

Neither the $C_6H_6^{\bullet-}$ free ion or its ion-pairs are expected to have long-term stability at room temperature, but may be important intermediates in chemical reactions under strongly reducing conditions, such as the Birch reduction.[19] $C_6H_6^{\bullet-}$ and its derivatives act as superexchange intermediates[20] in electron transfer reactions, but the energies required to form them are still not clear. It has been extensively examined theoretically [21] and radical anions of benzene derivatives paired with alkali cations complexed by crown ethers can be used as synthetic agents or to separate isotopes of the parent molecules.[22] Benzene reacts with solvated electrons (e^-_s) in water and alcohols at rates well below the diffusion control limit to form cyclohexadienyl radicals.[11,14] Benzene also reduces the initial yield of solvated electrons in pulse radiolysis of alcohols,[4,23] reportedly by capture of electrons before they are solvated. $C_6H_6^{\bullet-}$ is presumably an intermediate, but it has not been observed.

This paper reports observations by pulse radiolysis of $C_6H_6^{\bullet-}$ in THF solution, where it is found to be in equilibrium with solvated electrons. The observed equilibria provide energetics for both the free ions and ion pairs with Na$^+$.

Experimental Section

While sample preparation, experimental setup, data collection, and analysis have been described in detail elsewhere,[24,25] a brief overview of the experimental procedures will follow. HPLC grade benzene (C_6H_6), toluene (C_6H_5Me), tetrahydrofuran (THF), fluorobenzene (C_6H_5F), and 1.4-difluorobenzene, ($C_6H_5F_2$) were obtained from (Aldrich) and purified by fractional distillation under nitrogen. The purified benzene and THF were then transferred to storage flasks and degassed via pump-freeze−thaw and stored over NaK. THF$_{d8}$ (Aldrich) was degassed via pump-freeze−thaw and stored over NaK until used. Sodium

TABLE 1: Measured Equilibrium Constant, K_{Eq}, and Free Energy Change, $\Delta G° = -RT \ln K_{Eq}$, for the Reaction of Solvated Electron with Benzene in THF (Reaction 1)

| T (C)	K_{eq}	$\Delta G°$ (meV)	T (°C)	K_{eq}	$\Delta G°$ (meV)
−80	65.7 ± 6.6	−70 ± 2	−20	1.09 ± 0.1	−2 ± 2
−70	44.1 ± 4.4	−66 ± 2	−10	0.85 ± 0.9	4 ± 2
−60	20.1 ± 2	−55 ± 2	0	0.66 ± 0.07	10 ± 2
−50	7.87 ± 0.8	−40 ± 2	+10	0.38 ± 0.04	24 ± 2
−40	4.2 ± 0.4	−29 ± 2	+25	0.211 ± 0.02	40 ± 2
−30	2.5 ± 0.25	−19 ± 2	+40	0.17 ± 0.02	48 ± 3

tetraphenylborate (NaBΦ₄, Dojin, 99.8%), was used without further purification.

Solutions of benzene or substituted benzenes in THF were prepared and placed in quartz spectrophotometric cells capped with white rubber septa and deaerated by bubbling with argon. For experiments at other than ambient, a temperature-controlled sample block cooled by flowing nitrogen gas was used.[25] Chemical events after generation of excess electrons by 30 ps, 20 MeV electron pulses from Argonne's linear accelerator were monitored by transient absorption. The pulse radiolysis technique creates short pulses of high energy electrons. While those primary electrons pass completely through and exit the spectrophotometric cell, each produces ∼10⁴ ionizations in the cell that result in a few μM of thermalized solvated electrons (e^-_s), and a corresponding number of cations. In THF the cations decompose to radicals and solvated protons. The e^-_s and anions formed therefrom react with the protons and radicals. These reactions are measured and accounted for in the measurements.[24,25] Optical detectors included a biplanar phototube (Hamamatsu, R1328U-03), silicon (EG&G FOD-100, OEL CD10) Ge and InGaAs (Germanium Power Devices Gap500L) photodiodes, and a photomultiplier tube (Hamamatsu, R928), depending on the observation wavelength. The signals were collected with Tektronix SCD5000, 7912, and 680b digitizing oscilloscopes.

Values of K_{eq} were obtained by simultaneously fitting the multiple data sets for the series of concentrations at a single wavelength, 1507 or 2000 nm, where solvated electrons in THF absorb strongly and $C_6H_5R^{\bullet-}$ absorbs little. The fits utilized solutions[24] to the appropriate kinetic mechanisms applied within a nonlinear least-squares fitting program developed by Jonah.[26]

Results

Reactions in THF without Inert Ions. The solvated electron in THF has a broad intense absorption in the near-infrared.[27] At room temperature high concentrations of benzene reduce the absorption almost uniformly across the near-IR. The amount of reduction is in accord with an equilibrium expression:

$$e^-_s + C_6H_6 \rightleftharpoons C_6H_6^{\bullet-} \qquad (1)$$
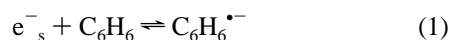
$$K_{eq}(e^-_s, C_6H_6\bullet^-)_{THF} = \frac{[C_6H_6^{\bullet-}]}{[e^-_s][C_6H_6]} \qquad (2)$$

The equilibrium constant of eq 2 for benzene (R = H) at 25 °C is small, $K_{eq} = 0.22$ M⁻¹. No kinetics of approach to equilibrium could be observed in experiments with 0.25 ns time resolution; apparently the reaction was at or very near equilibrium at the earliest observation. By themselves, these experiments do not convincingly demonstrate that an equilibrium is occurring; even at 4 M benzene, where the solution is ∼ 40% benzene by volume, more than half the solvated electrons remain and the decrease in absorbance of e^-_s with increasing [C₆H₆], from

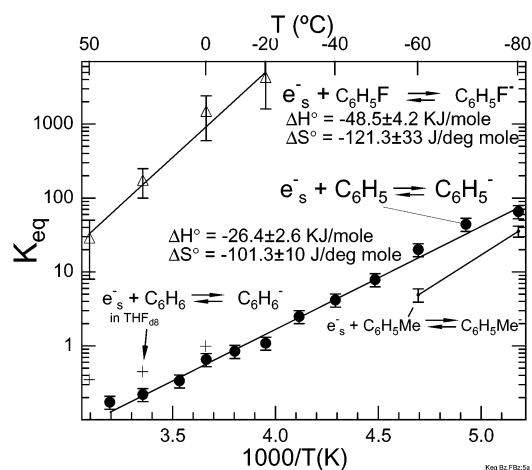**Figure 1.** Temperature dependence of equilibrium constants for reaction of solvated electrons with benzene (C₆H₆), fluorobenzene (C₆H₅F), and toluene (C₆H₅Me) in THF and with benzene in THF$_{d8}$.
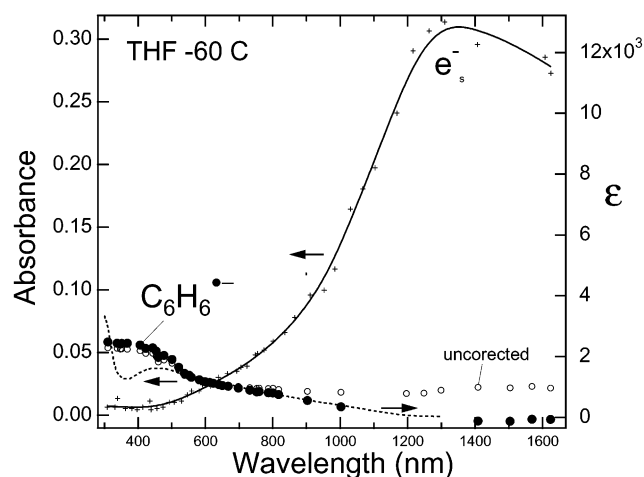

Figure 2. Absorption spectrum of benzene free radical anion in THF at −60 °C. Absorbance in a solution of 0.433 M benzene at 45±10 ns after accelerator pulse (○). The spectrum of solvated electrons generated in neat THF under the same conditions (+). The corrected spectrum for C₆H₆•⁻ (●) after subtraction of a contribution from solvated electrons according to the measured equilibrium constant. The spectra refer to the left axis. The dashed line is Shida's spectrum of C₆H₆•⁻ at 77 K[2] referred to the right axis, the range of which was set to approximately match the two spectra of C₆H₆•⁻.

which K_{eq} was measured, could be adequately described by almost any decreasing function.

When the temperature is reduced the equilibrium shifts to the right reaching $K_{eq} = 65$ M⁻¹ at −80 °C (Table 1 and Figure 1). Similar equilibria were also observed with toluene and fluorobenzene, and with benzene in perdeuterated THF. While equilibrium constants with fluorobenzene were much (>100 times) larger, the observed entropies were similar.

Figure 2 shows the absorption spectrum of the benzene radical anion at −60 °C. The absorbance due to solvated electrons was subtracted. The spectrum is similar to that reported in frozen MTHF (2-methyltetrahydrofuran) glass,[1,2,28] but is even more featureless. It also resembles the spectrum obtained by alkali metal reduction at reduced temperature.[8] The broadening at the higher temperature is typical of that seen by comparing the cryogenic spectra[2] with those obtained at room temperature for biphenyl[29] or various aromatic hydrocarbons.[29,30]

The rate constant for e^-_s +fluorobenzene was found to be $(2.6±0.9) \times 10^{10}$ M⁻¹s⁻¹ at 298 K. For toluene, like benzene, high concentrations (>0.1 M) were needed for appreciable
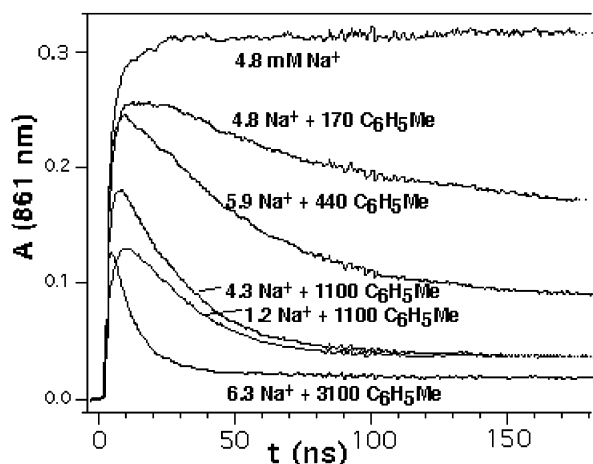
Benzene Radical Ion

J. Phys. Chem. A, Vol. 107, No. 12, 2003 **2035**

Figure 3. Transient absorbance at 861 nm in THF containing NaBΦ₄ without and with various concentrations of toluene (C₆H₅Me) at 298 K. Concentrations for each are given in mM.

TABLE 2: Measured Equilibrium Constants for Reaction of Solvated Electrons with Toluene

| T (°C)	$K_{eq}{}^a$	$\Delta G°$ (meV)
−80	35.6 ± 3	−59 ± 15
−60	4.9 ± 0.4	−29 ± 16

^{a} Measured at 0.1 M toluene.

TABLE 3: Measured Equilibrium Constants K_{eq} and Free Energy Change $\Delta G°$ for the Reaction of Solvated Electrons with Fluorobenzene (C₆H₅F) in THF and with Benzene (C₆H₆) in THF_D8

T (°C)	C₆H₅F, K_{eq}	C₆H₅F, $-\Delta G°$ (meV)	C₆H₆/THF_d8, K_{eq}	C₆H₆/THF_d8, $\Delta G°$ (meV)
−20	4.3 ± 2.7 × 10³	183 +11/−22		−183 +11/−22
0	1.5 ± 0.9 × 10³	172 +11/−22	0.99 ± 0.2	−172 +11/−22
+25	175 ± 75	133 +9/−14	0.45 ± 0.09	−133 +9/−14
+50	29 ± 21	94 +15/−36	0.35 ± 0.07	−94 +15/−36

capture of e⁻_s, and no approach to equilibrium could be observed at or near room temperature. Reaction of solvated electrons with 1,4-difluorobenzene was also studied, but no remaining solvated electrons could be observed at equilibrium so only a limit, $K_{eq} > 1 \times 10^5$ M⁻¹ was obtained, consistent with Holroyd's measurements in hexane and cyclohexane.[31]

Reactions in the Presence of Inert Ions. When sufficient sodium tetraphenylboron (NaBΦ₄) is present the solvated electrons are converted to ion-pairs, (e⁻_s,Na⁺), which have an intense absorption band at 890 nm ($\epsilon = 2.4 \times 10^4$ l mol⁻¹ cm⁻¹) and ∼2 μs lifetime.[29,32] Sufficient here means that enough Na⁺ is present to convert most e⁻_s to (e⁻_s,Na⁺). The very complete conversion (>99.9%) of e⁻_s to (e⁻_s,Na⁺) observed is expected on the basis of dissociation constants K_d(NaBΦ₄) = 8.52 × 10⁻⁵ M⁻¹ [33] and the much smaller K_d(e⁻_s,Na⁺) = 3 × 10⁻⁸ M⁻¹ measured by Szwarc and co-workers.[34] Figure 3 shows a set of time profiles of the absorbance at 861 nm in solutions of NaBΦ₄ containing different concentrations of toluene and Figure 4 shows spectra without and with toluene. In the presence of toluene the (e⁻_s,Na⁺) absorption band decays to a plateau dependent on [toluene]. Now reaction 1 is replaced by the ion-paired electron-transfer equilibrium (eq 3).

$$(e^-{}_s,Na^+) + C_6H_5R \rightleftharpoons (C_6H_5R^{\bullet-},Na^+) \quad (3)$$
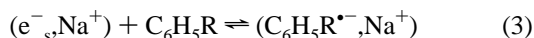
Similar equilibria were observed for reaction of (e-,Na⁺) with benzene and *tert*-butylbenzene. Table 4 reports equilibrium constants and rate constants for these reactions at room
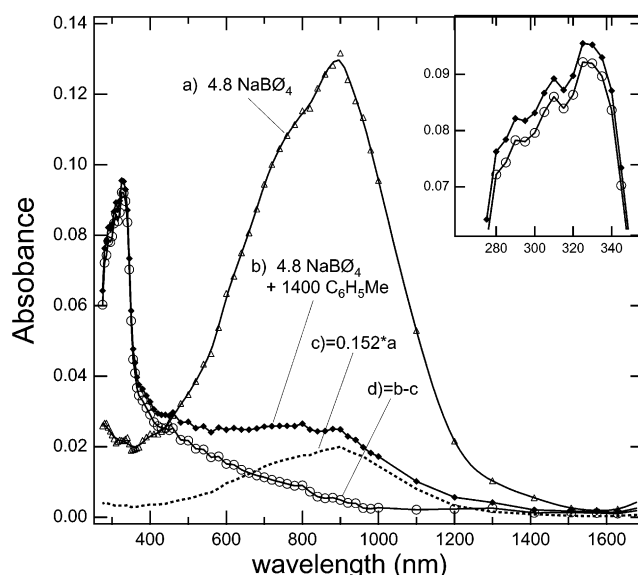

Figure 4. Transient absorption spectra at 300 ±150 ns after radiolysis of the samples in THF containing (a) 4.8 × 10⁻³ mol L⁻¹ NaBΦ₄, and (b) 1.4 mol L⁻¹ toluene (C₆H₅Me) and 4.2 mM NaBΦ₄ at 298 K. The contribution of (e⁻,Na⁺) remaining is shown (c). The spectrum (d) obtained by subtraction of (c) from (b) indicates (C₆H₅Me•⁻,Na⁺) and other species described in the text.

temperature, along with comparisons to gas phase and equilibria among ion pairs. The difference between the free energy change for reactions 3 and 1 yields the difference between the dissociation free energies $\Delta G°_d$ for ion pairing:

$$\Delta G°[(e^-{}_s,Na^+)+C_6H_5R] - \Delta G°[e^-{}_s+C_6H_5R] =$$
$$\Delta G°_d(e^-{}_s,Na^+) - \Delta G°_d(C_6H_5R^{\bullet-},Na^+) \quad (4)$$

From the measured equilibria and Szwarc's reported dissociation constant for (e⁻_s,Na⁺)[35] the dissociation constant for (C₆H₅R•⁻,Na⁺) ion pairs is obtained.

A peak at 330 nm in Figure 4 contains contributions from (Na⁺,C₆H₅Me•⁻) but probably also contains contributions from radicals formed from toluene⁺, some of which is formed by direct ionization at the high concentration used.

Discussion

Given the very negative (−1.17 eV) electron affinity of benzene, observation of free benzene anion may seem remarkable, as is the temperature dependence of the equilibrium constants. Before discussing these it is appropriate to consider the validity of the measurements.

Measured Equilibria. Positive ions of benzene or toluene readily complex with an additional benzene (toluene) molecule to form dimer cations having strong, distinct absorption bands at ∼900 nm.[36] While the negative ions have not been reported to form similar dimer anions, and the data in Figure 1 appear to indicate simple equilibria (reaction 1), large, 0.5−4 M, concentrations of benzene were used at room temperature and above. The possibility that aggregation of benzene or toluene could distort the apparent equilibria should be considered. That the equilibria are valid and not significantly perturbed by aggregation are indicated by the following observations: (1) The Arrehnuis plots in Figure 1 are linear. (2) The very negative entropies are similar within experimental uncertainty for benzene and fluorobenzene, although the concentrations used for fluorobenzene were more than 100 times smaller. (3) $\Delta H°$ is more negative for fluorobenzene by 22.1 kJ/mol = 0.23 eV, consistent

TABLE 4: Equilibria and Rate Constants for Reactions $(e^-_s, Na^+) + C_6H_5R \rightleftharpoons (C_6H_5R^-, Na^+)$ in THF Containing $NaB\Phi_4$ at 298 $\pm$ 3 K with Comparisons to Similar Reactions of Biphenyl and Naphthalene

	C_6H_6	C_6H_5Me	C_6H_5t-Bu	biphenyl	naphthalene
K_{eq} (L/mol)	14 ± 2	6.5 ± 0.5	0.57		
$\Delta G°$ (meV)	-68	-48	$+14$		
$K_d(C_6H_5R^{•-}, Na^+)$ (L/mol$^-$)	$4.5 \times 10^{-10\,a}$			$1.15 \times 10^{-6\,b}$	$1.5 \times 10^{-7\,b}$
$-EA^c$ (eV)	1.15	1.11	1.06		
$\Delta G°(C_6H_5R^{•-}+C_6H_6)$ (meV) ^{d}	0	-22	-70		
k (L/mol s)	$(2 \pm 1) \times 10^7$	$(3 \pm 0.5) \times 10^7$	$(5 \pm 2) \times 10^6$	$5.5 \times 10^{9\,e}$	$1.0 \times 10^{10\,e}$

^{a} From $\Delta G°$ measured here and $K_d(e^-_s, Na^+) = 3 \times 10^{-8}$ L/mole .[34] ^{b} From Slates and Szwarc.[52] ^{c} Electron affinities in the gas phase.[12,53] ^{d} Free energy differences $(C_6H_5R^{•-} + C_6H_6 \rightarrow C_6H_5R + C_6H_6^{•-})$ at 173 K in the presence of Na^+ and K^+ cations measured by Lawler and Tabit.[54] ^{e} Measured by Bockrath and Dorfman.[29]

with the 0.26 eV difference in gas-phase electron affinities.[12] (4) The spectra are linear combinations of just two bands, the strong NIR band of the solvated electron and the weak absorption of $C_6H_6^{•-}$. The data are fully consistent with the simple equilibrium described by eq 1.

Energetics and Equilibria. At 25 °C the equilibrium between free solvated electrons and $C_6H_6^{•-}$ in THF (reaction 1) slightly favors e^-_s ($\Delta G° = +40$ meV) for a standard state of 1 M. Itoh and Holroyd[5] extrapolated measurements at high pressures in n-pentane to estimate similar energies at 1 atm ($\Delta G° = +70$ meV for benzene and $+130$ meV for toluene). The temperature dependence of K_{eq} indicates that the reaction is moderately exothermic, $\Delta H° = -26.3$ kJ/mol (-273 meV). This is remarkable because the same reaction would be endothermic by ~ 1 eV in the gas phase, according to measurements of electron transmission spectroscopy.[12,13] The temperature dependence data also indicate that a large reaction entropy (-101 J/deg mole, a statistical factor of 2×10^5) strongly favors e^-_s counterbalancing the negative $\Delta H°$. How can we understand the large difference between gas and solution phase energetics?

The large negative entropy changes found here are typical for electron transfer of solvated electrons. Entropy changes near to or larger than 100 J/deg mole have been reported for reactions of solvated electrons in hydrocarbons,[31,37] ammonia,[38,39] and water.[40] Entropy is not a direct observable in the measurements reported here. The actual observation is that $\Delta G°$ depends on temperature, e.g., d$(\Delta G°)$/d$T = -101$ kJ/mol for reaction of solvated electrons with benzene. In chemical reactions $\Delta H°$ is often nearly independent of temperature, so observations that d$(\Delta G°$/d$T) \neq 0$ are probable indicators of an entropy change. Therefore the right-hand approximation in eq 5 is commonly applied.

$$\frac{d(\Delta G°)}{dT} \cong \frac{d(\Delta H°)}{dT} - \Delta S° \cong -\Delta S° \quad (5)$$

Entropy changes are usually considered responsible for the very negative values of d$(\Delta G°$/d$T)$ in reactions of solvated electrons. They are thought to arise from a large number of states available to the electron in a disordered liquid,[31] or in terms of the structure-breaking nature of the solvated electron[39–41] and related concepts.[42] Negative entropy changes might also arise because reaction 1 combines two species into one. Association process are known to produce large negative entropy changes due to loss of translational and rotational degrees of freedom,[43] although Han and Bartels[40] concluded that translational entropy of electrons was small in water. While no one of these sources of entropy change seems likely to fully account for the large observed values, sufficient uncertainty surrounds the estimation of each that taken together they may explain the observations.

Nevertheless we wish to call attention to another possibility. Equation 5 contains a second term, d$(\Delta H°$/d$T)$ that provides a
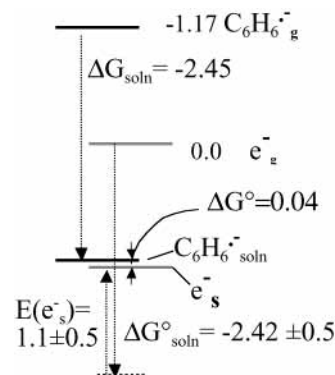

Figure 5. Estimated energetics for conversion of $C_6H_6^{•-}$ and e^- from the gas phase to solvated species in THF based on the observed $\Delta G° = +0.04$ eV for reaction of e^-_s with benzene. From gas-phase energetics changes include solvent polarization (arrows pointing down) for both species and an enrergy, $E(e^-_s)$, principally due to kinetic energy of confining the electron (up arrow). The dashed line at the bottom of the figure corresponds to an (impossible) electron having no ground-state electronic energy but stabilized by solvation energy. While the value $E(e^-_s) = 1.1 \pm 0.5$ eV is a rough estimate, the sum $E(e^-_s) + \Delta G_{soln}(e^-_s)$ is much better determined (see text).

plausible alternative explanation for the observation that $\Delta G°$ depends on temperature. This second term is *not* an entropy change, but has a similar effect on the equilibria. The source of this possible d$(\Delta H°$/d$T)$ is discussed in terms of eq 6, which considers the energetics of reaction 1 based on early descriptions of solvated electrons.[44,45]

$$\Delta G° = -EA(C_6H_5R) - E(e^-_s) + \Delta G_{soln}(C_6H_5R^{•-}) - \Delta G_{soln}(C_6H_5R) - \Delta G_{soln}(e^-_s) \quad (6)$$

EA is the gas-phase electron affinity, ΔG_{soln} are differential solvation free energies, and $E(e^-_s)$ is the energy for the solvated electron without solvent polarization. $E(e^-_s)$ is a positive (destabilizing) energy consisting of a kinetic energy due to confining the electron and local repulsions between the electron and solvent molecules. It may also contain an energy for creating a cavity at which e^-_s is localized. These energies are illustrated in Figure 5.

The EA(benzene) was measured to be -1.17 eV[12,13] and the solvent polarization energy, the difference, $\Delta G_{soln}(C_6H_6^{•-}) - \Delta G_{soln}(C_6H_6)$ in THF may be estimated to be -2.45 eV in a continuum dielectric as computed using the IPCM continuum model in Gaussian 98w[46] (B3LYP/6-31+G). The principal unknowns are $E(e^-_s)$ and $\Delta G_{soln}(e^-_s)$. From eq 6 the sum of these is $E(e^-_s) + \Delta G_{soln}(e^-_s) = 1.17 - 2.45 - 0.04 = -1.32$ eV. Calculations that have been performed on solvated electrons in MTHF can give insight.[44,45] Fueki, Feng, and Kevan[45] estimated individual contributions to the energy, giving the ground-state kinetic energy as ~ 1.1 eV. Taking this value as a

Benzene Radical Ion

J. Phys. Chem. A, Vol. 107, No. 12, 2003 **2037**

rough estimate for $E(e^-_s)$, $\Delta G_{soln}(e^-_s) \approx$ -2.42 eV. In this estimate $\Delta G_{soln}(e^-_s)$ is similar to that for $C_6H_6^{\bullet-}$. If so, entropies of solvation are likely to be similar.

So a reasonable description of the energetics for reaction of e^-_s with benzene is the following: The ~1.17 eV positive (endoergic) ehthalpy change in the gas phase is balanced in solution by an electronic energy $E(e^-_s)$ ~1.1 eV that accompanies localization of the electron, while solvent polarization energies for $C_6H_6^{\bullet-}$ and e^-_s are similar. This description explains the enthalpy change of reaction 1. A contribution to the apparent entropy may arise from the same source, due to basic differences between solvated electrons and molecular ions.

To understand the energetics of reaction 1, it is important to confront the present results with those of quantum calculations. The LUMO of THF lies 2.6 eV higher in energy than the LUMO of benzene according to HF/3-21G calculations, while the present measurements show that the free energy of e^-_s in THF is 40 meV below that of $C_6H_6^{\bullet-}$. The energetics do not support the idea that e^-_s is the anion, THF$^{\bullet-}$. Almost certainly the electron locates preferentially in the space *between* the THF molecules. That space is scarce and becomes more so as density increases. Therefore the wave function of e^-_s and the energy $E(e^-_s)$ must depend on density. By contrast the wave functions for electrons in molecular anions, such as $C_6H_6^{\bullet-}$, are largely confined within the benzene molecule and therefore have a spatial extent defined by the size of the molecule; they will change little with density and therefore with temperature. Therefore while increased density will slightly stabilize both e^-_s and molecular anions such as $C_6H_6^{\bullet-}$ due to increased solvent polarization, e^-_s will also experience a substantial destabilization. Could the effect of density on the energy of e^-_s account for the observed temperature dependence of $\Delta G°$?

The density of THF changes by ~10% over the 120° range studied here. For a 10% density change induced by application of pressure in hexane, Chen and Holroyd[47] found equilibria between solvated electrons and butadiene anions to shift by 0.1 eV. The size of that shift with density is sufficient to fully account for the apparent "entropy" change found here. While the shift was attributed to electrostriction around the anions,[47] it could be plausibly attributed instead to changes in the electronic energy of e^-_s. So while there may be entropy changes associated with reaction 1, entropy may not be the whole story. The apparent entropy change may be partially or even mostly due to a density-induced enthalpy change that results in the observed temperature dependence of $\Delta G°$.

Equilibria in the Presence of Na$^+$. The equilibria are shifted to the right when the species are paired with Na$^+$. For both benzene and toluene, the ions (Na$^+$,$C_6H_6^{\bullet-}$) and (Na$^+$,$C_6H_5Me^{\bullet-}$) are favored over (Na$^+$,e^-_s) at room temperature, while (Na$^+$,t-BuC$_6$H$_5^{\bullet-}$) is slightly disfavored. The dissociation constant K_d for benzene is very small as expected for a small molecule. Ion-pair distances calculated from the Fuoss equation[48] are 3.1, 4.6, and 3.8 Å for ion pairs of benzene, naphthalene, and e^-_s. In this sense the solvated electron is intermediate in size between benzene and naphthalene anions, in accord with calculations and measurements[45,49] on e^-_s.

The strong ion pairing of $C_6H_6^{\bullet-}$ with Na$^+$ explains why ion pairs of benzene and its alkyl derivatives have been observed previously while the free ions have not and why the spectra of the ion pairs (e.g., Figure 4) are readily observed even at room temperature.

The species (Na$^+$,e^-_s) with an absorption maximum near 860 nm has been described as an ion pair between Na$^+$ and the solvated electron.[29,34,35,50] Recently Barthel, Martini and Schwartz found the 860 band to be formed without delay upon photo-ejection of electrons from sodide (Na$^-$) in THF,[51] leading them to ask whether the species responsible for that band is better described as neutral sodium atom. If so the comments above on the "size" of the solvated electron should be dismissed. On the other hand spin−echo estimates of the size of e_s^- are in good accord with its measured ion-pairing energy[34] with Na$^+$, a fact also supported by the equilibria observed here. Therefore the traditional species, (Na$^+$,e_s^-), in which an electron sits beside an Na$^+$, is expected to have an energy close to that observed here. If the species observed at 860 nm is really Na atom, its energy must be only slightly below that of the pair (Na$^+$,e_s^-). Barthel et al. did note that a possible alternative explanation remains to be investigated.[51]

Conclusions

While the solvated electron might be considered the ultimate reducing agent in a given solvent, the free radical anion of benzene in THF solution is actually a slightly stronger reducing agent. Its high energy makes it difficult to observe, but its equilibrium with solvated electrons has now been measured. Whereas $C_6H_6^{\bullet-}$ has a much (1.17 eV[12,13]) higher energy than e^- in the gas phase, $C_6H_6^{\bullet-}$ and e^-_s have similar energies in THF solvent. The similarity arises because $C_6H_6^{\bullet-}$ is stabilized ~-2.5 eV by solvent polarization, whereas e^-_s is stabilized by a sum of solvent polarization and ground-state electronic energy $\Delta G_s(e^-_s) + E(e^-_s)$. While there is uncertainty in both $E(e^-_s)$ and $\Delta G_s(e^-_s)$, the sum $E(e^-_s) + \Delta G_s(e^-_s) = -1.32$ eV. With a reasonable estimate based on calculations,[45] $E(e^-_s) \sim 1.1$ eV, $\Delta G_s(e^-_s) = -2.4$ eV, which is similar to the solvent polarization energy for $C_6H_6^{\bullet-}$.

Free $C_6H_6^{\bullet-}$ is slightly more stable than e^-_s at low temperature, but the equilibrium is reversed near or above room temperature where e^-_s is more stable. This explains why electrochemical measurements at room temperature observe reduction of the solvent, not benzene. Reduction potentials measured at reduced temperature[17,18] should give reasonable ($\pm$0.2 V) estimates for the reduction potential of benzene at room temperature, subject to corrections for entropy and ion pairing. The equilibria observed here fit $\Delta H° = -26$ kJ/mol, $\Delta S° = -101$ J/deg mole, suggest that $C_6H_6^{\bullet-}$ is favored by enthalpy and e^-_s is favored by a larger entropy. There are many possible sources for this entropy, but it is plausible that part, or perhaps most, of the apparent entropy change is really due to dependence of enthalpy on temperature, due to the effect of solvent density on the ground-state energy of e^-_s. If so, the enthalpy change at room temperature may actually favor e^-_s. Ion pairing with Na$^+$ shifts the equilibrium to favor $C_6H_6^{\bullet-}$, even at room temperature: $C_6H_6^{\bullet-}$ forms a stronger ion-pair with Na$^+$ than does e^-_s. In this sense the size of e^-_s is intermediate between that of $C_6H_6^{\bullet-}$ and naphthalene$^-$.

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