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Effect of Isotopic Substitution on Association with the Sodium Counterion

Cheryl D. Stevenson,*,† **Eugene P. Wagner II, and Richard C. Reiter**

Department of Chemistry, Illinois State University, Normal, Illinois 61761

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EPR studies have shown that in tetrahydrofuran the associative interaction between the sodium cation and an organic anion is perturbed upon replacement of the protons in the anion with deuteriums. Specifically, the sodium hyperfine coupling constant for the naphthalene anion radical is increased upon perdeuteriation of the naphthalene. This may, in part, be due to a perturbation of the vibrational energies of the anion, but thermal dependence seems to indicate that the equilibrium constant controlling the dissociation of the tight ion pair to the solvent-separated ion pair ($\mathrm{Na^+,C_{10}H_8{}^{\bullet-} = Na^+//C_{10}H_8{}^{\bullet-}}$) is also affected ($K$(perprotiated)/$K$(perdeuteriated) = 0.974 ± 0.005 at 298 K). The van't Hoff plots show that the enthalpy of this dissociation may be as large as 120 J/mol more exothermic for the isotopically light system. Due to the large gyromagnetic ratio of the sodium nucleus, this system is ideal for observation of this effect.

Introduction

The most fundamental interaction in inorganic chemistry is the Coulombic attraction between a positive metal ion and a negative species. Under conditions where this interaction is mediated by a solvent, the phenomenon is called ion association.[1] The importance of this interaction coupled with our earlier observation that the attenuation of solution electron affinities resulting from isotopic substitution[2] is dependent upon the solvating media[3] led us to investigate the possibility that isotopic substitution may alter the degree to which anions and inorganic cations associate in a given medium.

Even though it has not been reported previously, we anticipated that the EPR measured hyperfine splitting constant from a metal cation associated with an anion radical might be altered via isotopic substitution in the organic anion radical. This isotopic perturbation in the relationship between the two ions might result from the expected change in the zero-point vibrational energy between the ions, which should take place upon isotopic substitution in the anion. This in turn would alter the thermodynamic equilibrium constants controlling the concentrations of tight, loose, and free solvated ions.

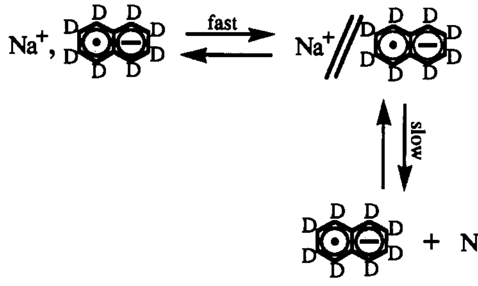
In systems where the various ion pairs are in rapid equilibrium on the EPR time scale, only the weighted average EPR coupling constant for the metal ion is observed. An isotopic perturbation of this value can result from a change in the metal ion coupling constant for either or both of the distinct species and/or an alteration of an equilibrium constant. However, according to the Born–Oppenheimer approximation, neither the coupling constant for the tight ion pair nor that for the solvent-separated ion pair can vary with isotopic substitution. Within the framework of this approximation, the potential energy surface for the vibrational–rotational motions of a molecule is independent of the number of neutrons in the nuclei.[4]

One of the most well understood of ion-associated systems is that involving the alkali metal cations and the naphthalene anion radical, where EPR spectroscopy yields unambiguous information about the structure of the ion pair.[5] EPR measurements in tetrahydrofuran (THF) allowed Zandstra and Weissman[6] to observe the rapidly (on the EPR time scale) equilibrating tight and solvent-separated sodium ion pairs. The tight ion pair is reported to have a sodium coupling constant greater than 2.2 G while that of the solvent-separated ion pair is unmeasurably small.[7] In the fast-exchange region, where only a single EPR line is recorded for the tight ion pair ($\mathrm{Na^+,C_{10}H_8{}^{\bullet-}}$) and the solvent-separated ion pair ($\mathrm{Na^+//C_{10}H_8{}^{\bullet-}}$), a signal for a third species was observed.[8] This third resonance has been attributed to the free solvated anion ($\mathrm{Na^+ + C_{10}H_8{}^{\bullet-}}$), which is undergoing slow exchange on the EPR time scale.[7,8]

Here we report that the replacement of the hydrogens by deuteriums in the naphthalene anion radical ($\mathrm{C_{10}D_8{}^{\bullet-}}$ vs $\mathrm{C_{10}H_8{}^{\bullet-}}$) results in a measureable change in the observed sodium hyperfine splitting constant (a_{Na}) in one of the most common anion radical solvents, tetrahydrofuran (THF). Further, temperature dependence studies indicate that the isotopic perturbation upon a_{Na} is due to a change in the equilibrium constant controlling the relative concentrations of $\mathrm{Na^+,C_{10}H_8{}^{\bullet-}}$ and $\mathrm{Na^+//C_{10}H_8{}^{\bullet-}}$.

Results and Discussion

When a freshly distilled sodium mirror is exposed to perdeuteriated naphthalene dissolved in THF under vacuum, the solvated sodium ion and anion radical are generated and exist in at least three different states of ion association. These include the free solvated ions ($\mathrm{Na^+ + C_{10}D_8{}^{\bullet-}}$) as well as $\mathrm{Na^+//C_{10}D_8{}^{\bullet-}}$ and $\mathrm{Na^+,C_{10}D_8{}^{\bullet-}}$. Upon EPR analysis, the resulting solution exhibits a time-averaged sodium hyperfine splitting ($a_{\mathrm{Na(D)}}$ = 1.038 G) at 298 K (Figure 1). This observed sodium splitting is controlled by the overall degree of ion association between the anion radical and the sodium cation (reaction 1)[6,8] and is a weighted average



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[†] This author previously published under the name Gerald R. Stevenson.

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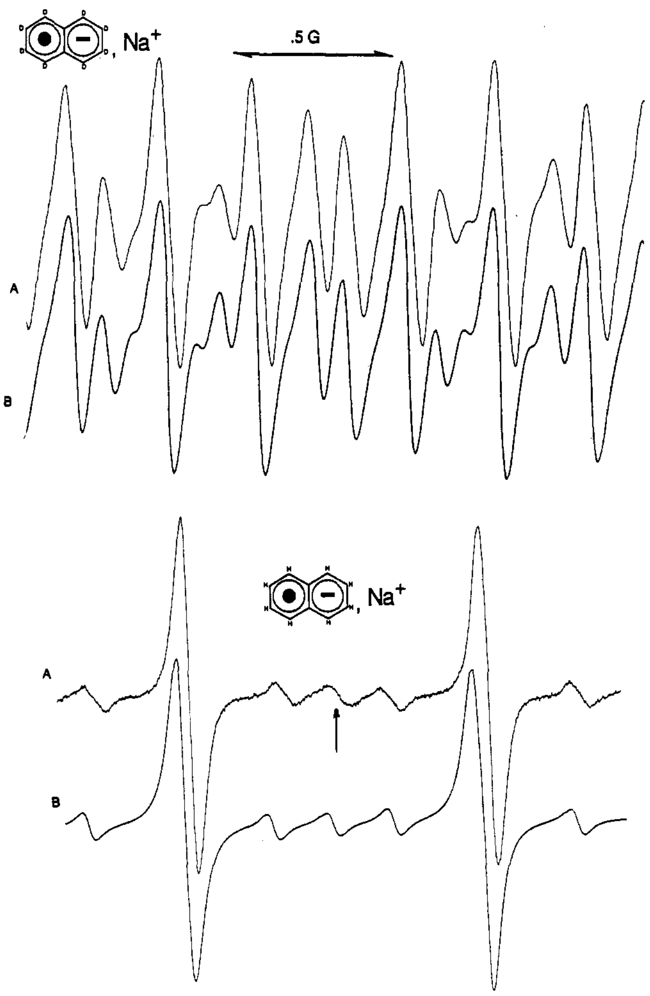

Figure 1. Bottom: (A) central portion of the EPR spectrum of the anion radical of naphthalene at 269 K generated via sodium reduction in THF and (B) the computer simulation where a_{Na} = 0.920 G and peak to peak line width = 0.043 G. This spectrum contains a 2.5% contribution from the free solvated anion radical. At this lower temperature, the solvated free ion is clearly observable. Over this scan range only the center line, indicated by the vertical arrow, is observed for this species. Top: (A) central portion of the EPR spectrum of the anion radical of perdeuteriated naphthalene at 298 K generated via the sodium reduction in THF and (B) the computer simulation where a_{Na} = 1.038 G and peak to peak line width = 0.050 G.

(two-site model) of those for the solvated tight or "contact" ion pair (a_{Na}'') and the solvent-separated ion pair (a_{Na}') (eq 2).[8-10]

$$a_{Na} = \frac{a_{Na(D)}''[Na^+,C_{10}D_8^{\bullet-}] + a_{Na(D)}'[Na^+//C_{10}D_8^{\bullet-}]}{[Na^+,C_{10}D_8^{\bullet-}] + [Na^+//C_{10}D_8^{\bullet-}]} \quad (2)$$

The free solvated ion undergoes slow (on the EPR time scale) exchange with the two types of ion pairs and is observed simultaneously as a separate radical species (Figure 1). Thus, it should not be included in the weighted-average equation. The sodium coupling constant for the free ion is zero, and that for the solvent-separated ion pair is also very close to zero, while that for the contact ion pair is reported to be larger than 2.2 G.[7]

Careful inspection of the EPR spectra of samples of the anion radicals of naphthalene and perdeuteriated naphthalene reduced with sodium metal in THF clearly shows that the sodium coupling constant for the heavy anion radical is larger than that of the normal (light) anion radical at 298 K by 24 ± 4 mG (data displayed in Figure 2). The standard deviation is taken from over 50 measurements involving several independently generated anion radical solutions. This coupling constant difference, which reaches a maximum of 35 mG at 281 K, means that the fundamental interaction between the anion and metal cation is altered due to the presence of the eight "extra" neutrons in the anion. From Figure 2 it appears that a_{Na} values for the perdeuteriated and perprotiated systems approach one another at the high-temperature extreme. This would imply that $a_{Na(H)}'' \approx a_{Na(D)}''$, which is in accord with the expectations of the Born–Oppenheimer approximation. At the low-temperature extreme, the metal splitting approaches zero, and consequently $a_{Na(H)}' \approx a_{Na(D)}'$. Therefore, the fact that $a_{Na(H)} \neq a_{Na(D)}$ must, at least in part, be due to a perturbation of the equilibrium constant controlling the degree of ion association (K_{eq} for $Na^+,C_{10}H_8^{\bullet-} \rightleftharpoons Na^+//C_{10}H_8^{\bullet-}$).

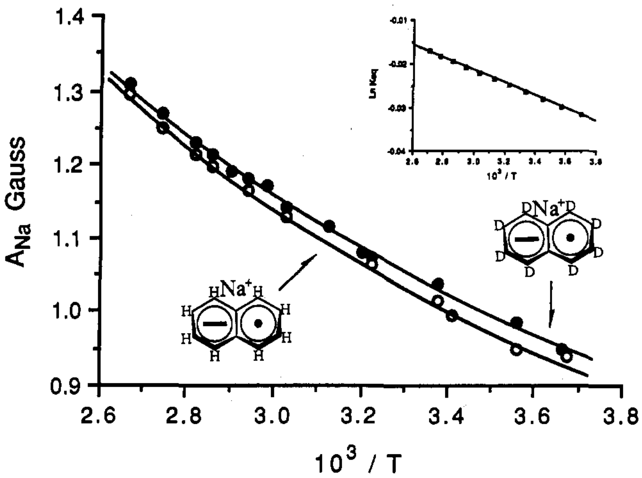

Figure 2. Plots of the observed sodium hyperfine coupling constant vs the reciprocal of the temperature. The curves are fit to second-order polynomials ($y = 3.500 - 1.172x + 0.130x^2$ and $y = 3.565 - 1.217x + 0.136x^2$) for $C_{10}D_8^{\bullet-}$ and $C_{10}H_8^{\bullet-}$, respectively, with a correlation constant of 0.998. Note that that the coupling constants converge as the temperature increases. At very low temperatures (not shown on this plot) they converge again, this time to zero. The insert is the van't Hoff plot generated from the polynomial expressions.

This means that K_{eq} for the reaction in which the sodium cation tightly associated with $C_{10}D_8^{\bullet-}$ and the sodium cation loosely associated with $C_{10}H_8^{\bullet-}$ are exchanged in terms of their mutual positions (reaction 3) is not unity. The equilibrium constant for this reaction is given by eq 4.

$$Na^+//C_{10}H_8^{\bullet-} + Na^+,C_{10}D_8^{\bullet-} \rightleftharpoons Na^+,C_{10}H_8^{\bullet-} + Na^+//C_{10}D_8^{\bullet-} \quad (3)$$

$$K_{eq} = a_{Na(H)}(a_{Na(D)}'' - a_{Na(D)})/a_{Na(D)}(a_{Na(H)}'' - a_{Na(H)}) \quad (4)$$

As pointed out by Hirota,[7] the reaction $Na^+,C_{10}H_8^{\bullet-} \rightleftharpoons Na^+//C_{10}H_8^{\bullet-}$ is shifted to the left with a consequent increase in the observed a_{Na} as the temperature is increased, and a_{Na}'' can be estimated via an extrapolation of the observed a_{Na} to very high temperatures. In order to facilitate this extrapolation, we plotted the observed a_{Na} for both the isotopically light and heavy anion radicals vs the reciprocal of the temperature over a 100-deg range (275–375 K, Figure 2). Both plots were curve-fit and extrapolated to $1/T = 0$ ($T \to \infty$). This process yields estimates of $a_{Na(H)}''$ and $a_{Na(D)}''$ which are both within experimental error of 3.5 and suggests (eq 4) K_{eq} to be 0.974 ± 0.005 at 298 K. The error involved in the extrapolation is too large to permit detection of a small difference that might exist between $a_{Na(D)}''$ and $a_{Na(H)}''$. Fortunately, however, the value of K_{eq} for reaction 3 is not sensitive to small deviations in the values of $a_{Na(D)}''$ and $a_{Na(H)}''$. In fact, as these values get very large, eq 4 reduces to $K_{eq} = a_{Na(H)}/a_{Na(D)}$.

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The possibility that a_{Na}' is not identical for the two radicals also exists. However, it has been well demonstrated that a_{Na}' is very close to zero.[7] Further, as long as the equilibrium constants are determined at temperatures where a_{Na} is much larger than a_{Na}', as is the case for all of the data presented in Figure 2, any error contribution to the above reported K_{eq} would be insignificant.[11] Consequently the error reported above in K_{eq} is a standard deviation propagated from the error in $a_{Na(D)} - a_{Na(H)}$ (24 ± 4 mG at 298 K).

The algebraic expressions for the two lines in Figure 2 provided averaged values for a_{Na} at the various temperatures, and these were used to evaluate the equilibrium constant at various temperatures for reaction 3 via eq 4. The data in Figure 2 yield values for the standard free energy, enthalpy, and entropy for reaction 3 of 65 ± 13 J/mol, 120 ± 18 J/mol, and 0.15 ± 0.08 J/(mol deg), respectively at 298 K. The errors in $\Delta H°$ and $\Delta S°$ were estimated by assuming the error in K_{eq} is invariant with the temperature.

Perdeuteriation is known to alter σ–π interactions and hence a_H/a_D ratios through out-of-plane vibrational zero-point energy perturbations.[4a,12,13] Thus, it seems logical that perdeuteriation would alter the zero-point energies of the vibrational modes involving the interaction between the metal cation and anion radical. This alteration of the relationship between the two ions could perturb the overall shape of the energy well describing the metal–anion interaction. This would be outside the scope of the Born–Oppenheimer approximation as it is applied to this system and hence would affect a_{Na}. This mechanism for changing the metal splitting upon perdeuteriation does not preclude the fact that K_{eq} for reaction 3 is decreased upon perdeuteriation. In fact, this may contribute to the thermodynamic destabilization of the solvent-separated ion pair relative to that of the tight ion pair in the sodium naphthalene anion radical. Regardless of the mechanism(s) involved, the nature of the thermal dependence of a_{Na} for the perdeuteriated and perprotiated systems (that is, their apparent convergence at the high- and low-temperature extremes) is consistent with the fact that K_{eq} for reaction 3 is measurably less than unity.

The large EPR signal intensity ratios for the perdeuteriated anion radical preclude the use of the outermost lines for the coupling constant measurements. Thus, the central 2-G portion of each spectrum was used. Most other perdeuteriated hydrocarbon anion radicals yield EPR patterns which are much more complex than that of $C_{10}D_8^{\bullet-}$ and thus do not give rise to EPR lines that are relatively free of overlap, from which the sodium splitting can be readily measured. The spectral appearance of $C_{10}D_8^{\bullet-}$ is extremely sensitive to metal splitting, making exceptionally precise measurements possible. Further, degenerate systems (i.e. benzene) cannot be studied in this manner as the line widths are too large. It is possible that the naphthalene system reported here is the only system where this effect of perdeuteriation upon ion association can be seen with present technology.

There exist several examples of inorganic reactions being significantly perturbed via ion association. For example, the rearrangement of the syn isomer of the sodium salt of the anion of tetraphosphorus seems to be inhibited by ion association,[14] and the lack of ion association totally prevents the reduction of ketones by sodium borohydride in aprotic solvents.[15] It follows that isotopic substitution of the anions involved in these and other reactions would also, at least slightly, perturb the chemistry of these reactions via its effect upon ion association.

In conclusion, this work indicates that the most fundamental interaction in inorganic chemistry, the Coulombic interaction between charged materials, is measurably perturbed by the presence of noncharged baryons (neutrons), and consequently their presence will also perturb all chemical transformations where ion association is involved.

Experimental Section

The anion radicals were generated exactly as previously described.[14] 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. For room-temperature measurements, samples of $C_{10}D_8^{\bullet-}$ were placed into the back cavity and samples of $C_{10}H_8^{\bullet-}$ into the front cavity. Spectra were then recorded several times, after which the samples were interchanged and the spectra recorded again. After recording of the complete spectra to demonstrate that the species being observed was indeed the naphthalene anion radical, the central portion of each spectrum was recorded using a 2-G sweep width. After correction for the cavity bias, this small scan range allowed the accurate determination of the sodium splitting. a_{Na} was found to be larger for $C_{10}D_8^{\bullet-}$ than for $C_{10}H_8^{\bullet-}$ regardless of cavity choice.

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