acid product of 1-benzyl-3-acetyl-1,4-dihydropyridine containing the elements of two molecules of the parent and one of water.

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Electron Paramagnetic Resonance Studies of Ion-Pair Equilibria[1]

Sir:

The temperature dependence of alkali metal splittings in aromatic anion radicals varies with the anion radical, the alkali metal, and the solvent.[2-5] There are, however, a number of systems in which the metal splittings change from the order of 1 gauss to almost 0 within a relatively small range of temperature. Sodium anthracene in 2-methyltetrahydrofuran (MTHF) and sodium 2,6-di-*t*-butylnaphthalene in tetrahydrofuran (THF) are such systems (Figure 1). We propose that a model involving an ion-pair equilibria can explain this sharp fall-off of metal splitting with temperature.

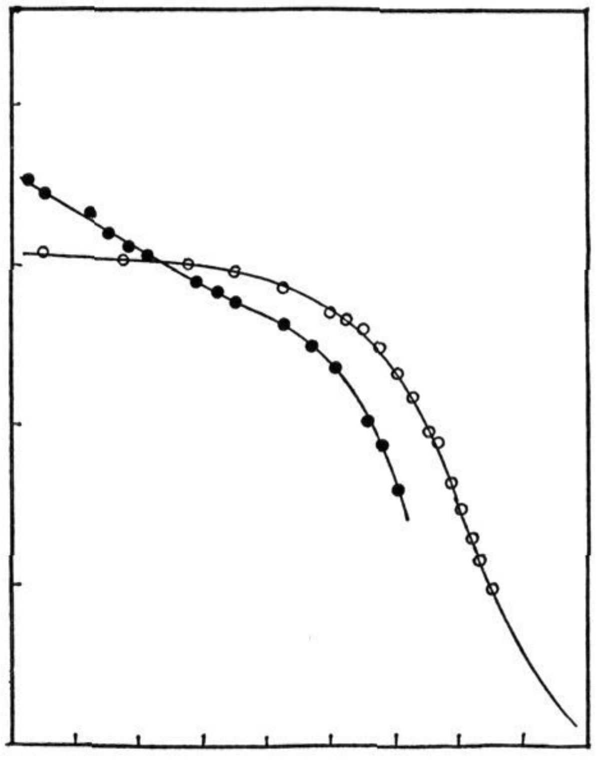
Figure 1. Temperature dependence of the sodium splittings: ○, sodium anthracene in MTHF and ●, sodium 2,6-di-*t*-butylnaphthalene in THF. The solid curve for anthracene in MTHF is the curve predicted by eq 1 with $\Delta H = -4.5$ kcal, $a_A = 1.55$ gauss, and $a_B = 0$.

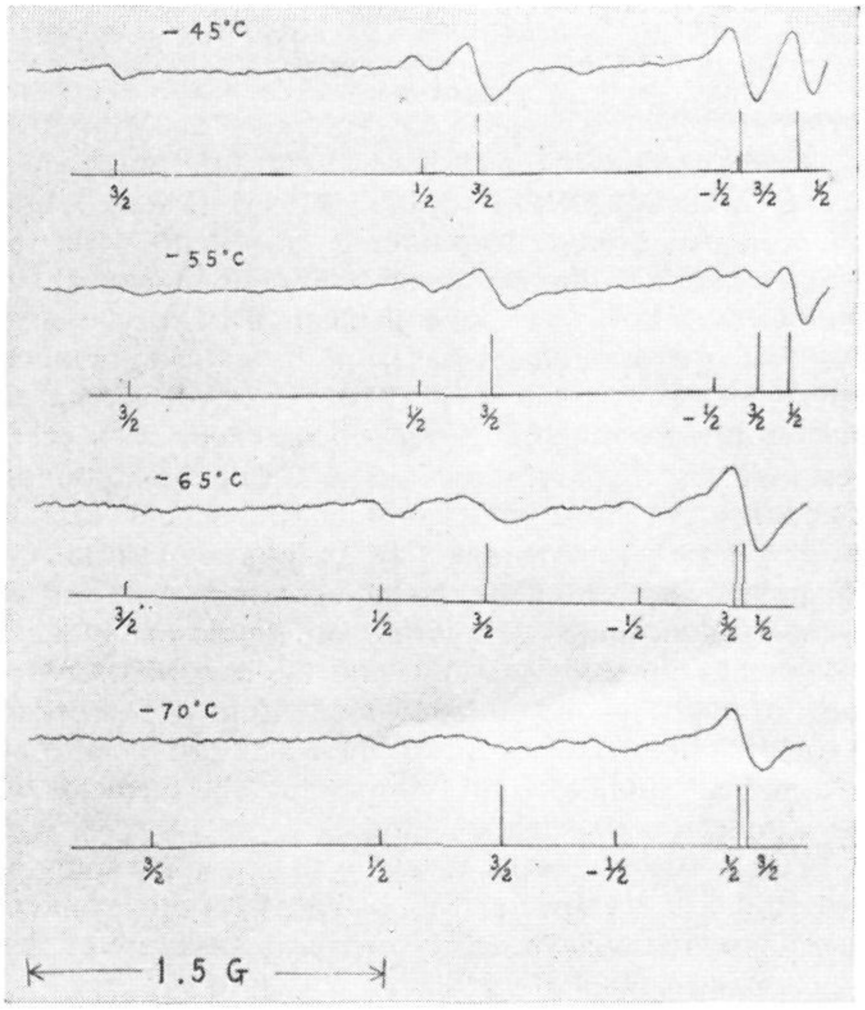

Figure 2. Temperature and M_Z^{Na} dependence of the line width of sodium anthracene.

Recently reported epr[6] and optical[7] spectra point out that two distinct types of ion pairs might exist. These ion pairs probably differ in their respective degrees of solvation and in the proximity of the alkali metal to the organic radical anion. One would expect different alkali metal splittings from two such species.

One possible method of interpreting the sharp temperature dependence of the alkali metal splitting is to consider a temperature-dependent rapid equilibrium between two structurally different ion pairs. We have investigated the temperature dependence of the line widths and the alkali metal splittings of sodium anthracene in MTHF and sodium 2,6-di-*t*-butylnaphthalene in THF, from 50 to −100° (Figure 1). The results obtained can be interpreted by the presence of a rapid equilibrium between two types of ion pairs, A and B.

We consider A and B to have two distinct coupling constants a_A and a_B. If P_A is the probability of finding form A and P_B the probability of finding form B, the equilibrium constant for interconversion of the two forms is given by

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$$K = \frac{P_B}{P_A} = \frac{t_B}{t_A}$$

where t_A and t_B are the lifetimes of the A and B forms.

In the limit of rapid exchange, the observed sodium splitting, $\bar{a}$, is given by

$$\bar{a} = P_A a_A + P_B a_B = \frac{a_A + K a_B}{1 + K} \qquad (1)$$

The contribution of the exchange to the line width of the sodium line can be determined by the standard procedure.[8]

$$\left(\frac{1}{T_2}\right)_{ex} = P_A{}^2 P_B{}^2 (W_A - W_B)^2 t_A (1 + K) \qquad (2)$$

In this equation W_A and W_B represent the resonant frequencies of the two types of ion pairs considered.

Values of K were determined for various temperatures through use of eq 1. We estimated the values of a_A and a_B to be 1.55 gauss and 0, respectively, for both systems under consideration. These values were obtained by extrapolating to the high- and low-temperature limits of the sharp fall-off region. The equilibrium between A and B is thought to be between tightly associated ion pairs, A, and loosely associated ion pairs, B.

A plot of log K *vs.* $1/T$ yields satisfactory straight lines for both systems. The slope of the lines gives $\Delta H = -4.5$ kcal for the anthracene case and -4.6 kcal for the di-*t*-butylnaphthalene case. The entropy change was estimated to be -22 eu for the anthracene case and -21 eu for the di-*t*-butylnaphthalene case.

The end of the epr spectrum of anthracene, at various temperatures, is shown in Figure 2 along with stick diagrams which show the position and relative intensities of the lines. Analogous results were obtained for di-*t*-butylnaphthalene. It is seen that at lower temperatures the line width depends on the magnetic quantum number of the sodium nucleus, $M_Z{}^{NA}$. Peaks with $M_Z{}^{NA} = \pm {}^3/_2$ broaden more rapidly than peaks with $M_Z{}^{NA} = \pm {}^1/_2$. Since $W_A - W_B$ is ${}^3/_2 \cdot a_A \gamma$ for peaks with $M_Z{}^{NA} = \pm {}^3/_2$ and ${}^1/_2 a_A \gamma$ for peaks with $M_Z{}^{NA} = \pm {}^1/_2$, this variation in line width is expected when the rate of conversion between A and B approaches the hyperfine frequency.

Through the use of eq 2, we have analyzed our data to give estimates of the lifetimes of species A and B. At $-55°$, t_A and t_B are 1×10^{-8} and 3×10^{-9} sec, respectively, for the anthracene case and 4×10^{-8} and 2×10^{-8} sec for the di-*t*-butylnaphthalene case.

The values of ΔH and ΔS obtained are similar in magnitude to those estimated for the dissociation of the sodium naphthalide ion pair. A similar discussion to that given in ref 2 can be used to explain these values. A large negative entropy change indicates a higher degree of ordering of solvent molecules in form B than in form A.

A rapid equilibrium between ion pairs and free ions cannot explain our observations, as rapid interchanges of different sodium nuclei would broaden out the metal splitting. We observe the spectra of the free ion as well, showing that a second equilibria between ion pairs and free ion is present.[2]

We feel that the linear change of log K with the reciprocal of temperature and the alteration in line widths strongly support the described mechanism. We are presently unwilling to commit ourselves on the mechanism leading to the slow increase in the sodium coupling constant in 2,6-di-*t*-butylnaphthalene at higher temperatures; however, we feel that slight changes in the structure of the tight ion pair could account for this variation. The presence of a second weakly associated ion pair may also account for Reddoch's[9] observations of slight changes in the proton coupling constants, upon dilution, in the anthracene radical anion.

Detailed studies on the structure and equilibria involving ion pairs and their connection to the kinetics of rapid electron-transfer reactions are now in progress and will be reported later.

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The Fluorides and Oxides of Helium and Neon[1]

Sir:

High-accuracy, many-electron, valence-bond wave functions have been obtained for HeO, HeF, NeO, NeF, and NeF_2. As shown in Figure 1, the potential energy curves for all of these species are repulsive (for NeF_2 and HeF_2 the linear molecule in a symmetric stretch is plotted). The method of forming the wave functions is the same as that previously reported for HeF_2,[2] and the NeF_2 result represents the highest precision quantum-mechanical solution yet achieved for a molecular system with this number of electrons.

The existence of HeO has been predicted by Jørgensen,[3] and Noyes[4] has predicted NeO and NeF. Their work employs reasonable and accepted chemical arguments. Considerable effort has been expended on attempts at the synthesis of HeF_2 and NeF_2 by a number of laboratories. It is also interesting to note that while the repulsive potential surfaces of Figure 1 can be roughly related to the high ionization potentials of helium and neon, the ordering of the curves does not follow the ordering of the ionization potentials (or electronegativities) of the participating atoms. All of these research efforts illustrate the general paucity and desirability of truly quantitative electronic structure calculations for much of chemistry.

The valence-bond wave functions have been constructed using the exact Hamiltonian with simultaneous

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