three moles of Tiron combine simultaneously with a gram-ion of Zr(IV). Also, the stabilizing effect of the additional ligand is not nearly as great when the chelate initially formed already involves combination of alkoxide anions with the metal. The considerable increase of stability observed in these chelates was cut down as the basicity of the auxiliary ligand was reduced.

Although in the case of the quadridentate ligands, NTA, HIMDA and HxG (N,N-dihydroxyethylglycine), it was found that the stabilities of the 2:1 complexes increase with the number of hydroxyalkyl groups, it is possible that in the complex of HxG, the number of such groups was already in excess of what is needed for optimum stability.

On the basis of the titration data given above, the stabilizing influence of bidentate ligands on Zr(IV) chelates of aminopolycarboxylic acids decreases in the order Tiron > chromotropic salt > acetylacetone > 8-hydroxyquinoline sulfonate > oxalate > 5-sulfosalicylic acid > *o*-phthalic acid. For five-membered rings the order of decreasing basicity of the anions is: Tiron > 8-hydroxyquinoline sulfonate > oxalate. For six-membered chelate rings, the order is chromotropic salt > acetylacetone > 5-sulfosalicylic acid. The position of alizarin-3-sulfonate in this series is not quite obvious from the analysis of the single titration curve available, but the data indicate that it may rank with Tiron and chromotropic salt, in accordance with its basicity.

The titration data given above, and the discussion of relative effectiveness of binding by bidentate ligands, offer evidence that 5-membered chelate rings are the most stable in zirconium complexes and that zirconium(IV) usually attains a characteristic coördination number of eight in its aqueous complexes under favorable conditions.

[CONTRIBUTION FROM THE LAWRENCE RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA, LIVERMORE, CALIFORNIA]

An Electron Spin Resonance Study of the Reaction of Pyridine with Potassium: The Formation of Bipyridyl Negative Ion[1]

BY RAYMOND L. WARD

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An electron spin resonance study of the product of the reaction of potassium metal with pyridine in 1,2-dimethoxyethane has been performed. Deuterated species have been synthesized and their negative ions prepared. A comparison of these paramagnetic species with the negative ion of 4,4′-bipyridyl indicates that pyridine has undergone a coupling reaction. Hyperfine coupling constants have been determined for all the magnetic nuclei, and the concept of spin density on the nitrogen atom is discussed.

Introduction

In recent years the study of solutions of aromatic hydrocarbon negative ions, positive ions and neutral free radicals, by electron spin resonance techniques, has yielded much information about the unpaired spin distribution in these molecules. Theoretical studies of these spin distributions have indicated that a σ-π exchange mechanism is responsible for the observed isotropic proton hyperfine interactions[2-5] and that an estimation of the spin density on a carbon atom is possible once the contiguous proton hyperfine interaction is known. The carbon spin density is estimated by the equation $A_{\mathrm{H}} = Q\rho$, where Q is a constant of magnitude -22.4 gauss.[6-7]

The hyperfine interaction of a nucleus in the ring of a free radical has been observed in only a few cases, by means of a complex isotopic synthesis[8,9] or by observing natural abundant isotopic splitting.[10] The study of heterocyclics, of which little has been reported, will yield information about the hyperfine interaction of magnetic aromatic ring nuclei.

We attempted to undertake a study of pyridine negative ion with the hope that a knowledge of its spin distribution would greatly help the work on more complex heterocyclics, as benzene negative ion did for aromatic hydrocarbons. Unfortunately, the paramagnetic product obtained when pyridine had reacted with potassium turned out to be not pyridine negative ion, but 4,4′-bipyridyl negative ion. Accordingly we have made a study of this paramagnetic species, determined coupling constants for all the magnetic nuclei and discussed the spin density at the nitrogen atom.

Results

In an attempt to prepare pyridine negative ion, an investigation of the reaction of potassium metal with pyridine in 1,2-dimethoxyethane was undertaken. Hydrocarbons, such as naphthalene or anthracene, react almost immediately with an alkali metal to yield a highly colored paramagnetic solution. The reaction with pyridine, however, is quite slow in comparison and must be performed at about -50 to $-70°$. It was observed that if a solution of pyridine in 1,2-dimethoxyethane was allowed to remain in contact with the alkali metal for only short periods of time, an intensely purple solution was obtained, which exhibited a copious hyperfine structure. If however the solution re-

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(1) This work was performed under the auspices of the U. S. Atomic Energy Commission.

(2) S. I. Weissman, *J. Chem. Phys.*, **25**, 890 (1956).

(3) H. M. McConnell, *ibid.*, **24**, 764 (1956).

(4) H. S. Jarrett, *ibid.*, **25**, 1289 (1956).

(5) R. Bersohn, *ibid.*, **24**, 1066 (1956).

(6) H. M. McConnell and D. Chesnut, *ibid.*, **28**, 107 (1958).

(7) T. R. Tuttle, Jr., and S. I. Weissman, *J. Am. Chem. Soc.*, **80**, 5342 (1958).

(8) T. R. Tuttle, Jr., and S. I. Weissman, *ibid.*, **25**, 189 (1956).

(9) T. R. Tuttle, Jr., *ibid.*, **32**, 1579 (1960).

(10) D. C. Reitz, F. Dravnieks and J. E. Wertz, *ibid.*, **33**, 1880 (1960).

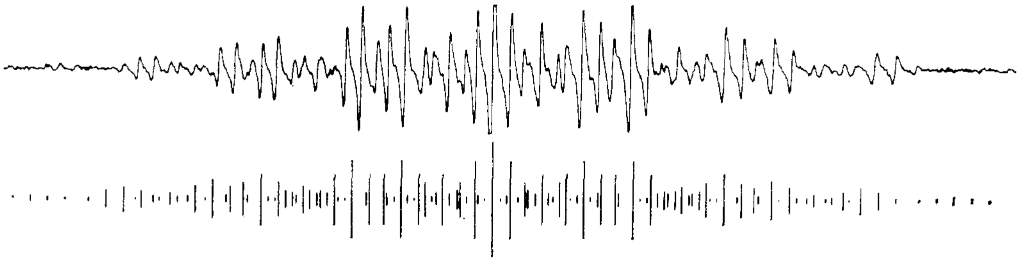

Fig. 1a (above).—dX''/dH vs. H for the reaction product of pyridine with potassium in 1,2-dimethoxyethane.
1b (below).—Calculated spectrum for 4,4′-bipyridyl negative ion.

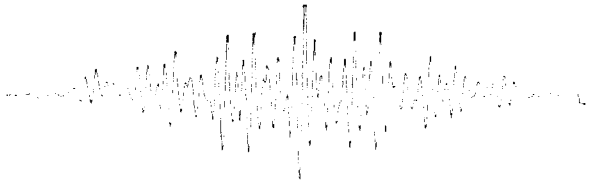

Fig. 2.—dX''/dH vs. H for the potassium salt of 4,4′-bipyridyl in 1,2-dimethoxyethane.

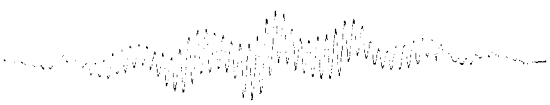

Fig. 3.—dX''/dH vs. H for the reaction product of pyridine-3-d_1 with potassium in 1,2-dimethoxyethane.

mained in contact with the alkali metal for relatively long periods of time, 5–10 minutes, a yellowish solution was formed which exhibited no resonance.

In the process of studying this paramagnetic solution, various deuterated species were synthesized and the negative ions prepared. An investigation of these deuterated species led to the unequivocal fact that the observed spectrum could not be accounted for by a simple unperturbed pyridine negative ion: two pyridine molecules must be assumed to be interacting in some manner. Observing that the γ-position did not exhibit a hyperfine interaction, we investigated 4,4′-bipyridyl negative ion and found an exact agreement of the spectra of this ion with the negative ion produced by the reaction of potassium with pyridine, under identical conditions of resolution. This indicated that first bipyridyl was formed and then its negative ion produced.

If the symmetry of the parent molecule, pyridine, had been retained in the formation of its negative ion, a maximum number of fifty-four lines would have been expected in dilute solution. The intensities of the proton hyperfine lines would have followed the usual binomial coefficient rule, and the magnitude of the splittings would be expected to be in the range of a few tenths to about five gauss. If nitrogen splittings had been observed, each of the proton lines would be split into a triplet of equal intensities. The approximate magnitude of these in-the-plane nitrogen splittings is not known, but it would be reasonable to assume that they are in the same range as the C^{13} splittings observed in naphthalene—7.1 gauss for the α-carbon and 1.2 gauss for the β carbon.[8,9]

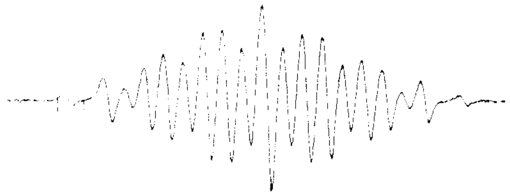

Fig. 4.—dX''/dH vs. H for the reaction product of pyridine-2,6-d_2 with potassium in 1,2-dimethoxyethane.

Although the spectrum of the reaction of pyridine with potassium (Fig. 1a) has approximately the correct number of lines for a completely resolved spectrum of pyridine negative ion, it is completely inconsistent with the spectra of the deuterated compounds. Rather, it is in perfect agreement with the spectrum of 4,4′-bipyridyl negative ion in Fig. 2. Assuming that this agreement is sufficient proof of the formation of bipyridyl negative ion, we can explain our results both for the unsubstituted and deuterated species.

Each of the possible monodeuterio compounds was synthesized according to the method of Bak, *et al.*,[11] and their negative ions were prepared. Pyridine-$4d_1$ negative ion does not exhibit a *para* position hyperfine interaction, and its spectrum is identical with that of 4,4′-bipyridyl negative ion in Fig. 2. The spectrum extends over 25.6 gauss. This lack of a *para* proton hyperfine interaction, and the equivalence of the 4,4′-bipyridyl negative ion spectrum, substantiate the conclusion that a coupling has taken place between two pyridine molecules.

The spectrum of pyridine-$3d_1$ negative ion appears in Fig. 3 and extends over 22.0 gauss. Comparing this spectrum and the one in Fig. 1a, it is estimated that the meta proton has a coupling constant of magnitude $|A_m| = 2.32$ gauss.

The negative ion of pyridine-2,6-d_2 also was prepared. Its spectrum appears in Fig. 4 and extends over 23.6 gauss. A comparison of this spectrum with Fig. 1a yields the magnitude of the *ortho* proton coupling constant. This value is $|A_0| = 0.45$ gauss.

All splittings were obtained by calibrating each spectrum with an auxiliary proton-resonance probe while the spectrum was being recorded. The values quoted are the results of at least three measurements.

The well-resolved spectrum in Fig. 1a of the product of the reaction of pyridine and potassium

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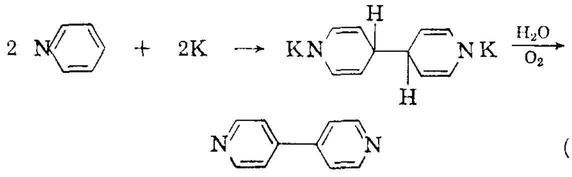
(11) B. Bak, L Hansen and J. Rastrup-Anderson, *J. Chem. Phys.*, **22**, 2013 (1954).

in 1,2-dimethoxyethane at −70° was recorded at room temperature, using a Varian 100-kc. spectrometer and a twelve-inch magnet. The spectrum in Fig. 2 of 4,4′-bipyridyl negative ion was recorded at room temperature using a 250-kc. spectrometer and a six-inch magnet. The remaining spectra, Figs. 3–4, also were obtained with the 250-kc. spectrometer and six inch magnet. The temperature of the samples was varied between −40 and +27° until the best resolution was obtained. Using the following values for the coupling

$$|A_N| = 3.6 \text{ gauss}$$
$$|A_0| = 0.45 \text{ gauss}$$
$$|A_M| = 2.32 \text{ gauss}$$

constants and assuming that 4,4′-bipyridyl negative ion was produced in the reaction, we calculate the spectrum which appears in Fig. 1b. The theoretical and observed spectra agree quite well.

It was suggested some time ago[12] that the reaction between pyridine and an alkali metal, in the absence of a solvent, proceeds according to the reaction



(1)

The author believes that this sequence of reactions has taken place in the present studies and that the deuterated species has proven the existence of 4,4′-bipyridyl negative ion as the final product. It should be noted, however, that according to equation 1, the formation of 4,4′-bipyridyl was presumed to take place upon addition of oxygen or water. The samples studied in this article were prepared *in vacuo* under stringent conditions designed to eliminate the presence of oxygen or water. But the possibility that a small amount of water or oxygen was present is not entirely eliminated. It is also possible that either potassium hydride was formed or a cleavage of the 1,2-dimethoxyethane took place. The exact mechanism of this last step is unknown to us at the present time.

Discussion

It is generally accepted that the mechanism for the isotropic hyperfine interaction, observed for protons in dilute solutions of free radicals, is a σ-π electronic exchange interaction at the position of the contiguous carbon atom.[2-5] This interaction produces an unpaired spin density at the position of the carbon atom as well as the proton. The magnitude of the proton isotropic hyperfine interaction has been related to the unpaired π-electron spin density at the position of the carbon atom[6] by the equation $A_H = Q\rho$, where Q is a constant of proportionality, −22.4 gauss, obtained from the over-all spread of the benzene negative-ion spectrum. Weissman and Adam[13] have defined the spin density at $\vec{r}_\alpha$ as the expectation value of the spin density operator

$$\sigma_{zk} \sum_k (\vec{r}_k - \vec{r}_\alpha)$$

where σ_{zk} is the Pauli spin operator for the z component of spin of the kth electron, and the sum is over all k electrons.

Weissman and de Boer[14] have applied the Hückel theory to aromatic hydrocarbon positive and negative ions and have been able to predict the ratios of coupling constants with reasonable accuracy in many cases. They assumed the relation, $A_H = Q\rho$, to hold, and determined a Q from the spread of each hyperfine pattern. They observed that Q was not a constant in the light of the Hückel theory but could vary for different hydrocarbons. The concept of negative spin density, which is not possible in the Hückel theory, has since allowed a constant Q to be used in the interpretation of their spectra. Recently McLachlan[15] has discussed many of these same hydrocarbon ions from a more sophisticated point of view and has been able to predict negative coupling constants for a few of the molecules. These negative coupling constants were suspected from the experimental results by de Boer and Weissman. McLachlan also showed that his treatment and the Hückel theory should agree in many cases.

It would be of value, due to its simplicity, if the Hückel theory could be adapted to the theory of heterocyclic negative ions in the same manner as it was for hydrocarbon ions. For heterocyclics the simplest change in the framework of the Hückel theory is to replace the nitrogen coulomb integral by the relation $\alpha_N = \alpha_C + \beta h$, and to vary h to agree with experiment. All exchange integrals, β, are assumed equal.

It seems reasonable to assume that the relation between proton coupling constant and π-spin density should hold for heterocyclics as well as hydrocarbons. But the presence of the nitrogen atom, to which no protons are attached, greatly increases the problem of estimating the spin density from experimental measurements. The same problem exists in estimating the spin density for the methyl position in triphenylmethyl.[13]

Recently, McLachlan, *et al.*,[16] have presented an extended theory of hyperfine interactions in aromatic radicals, which enlarges upon the relation $A_H = Q\rho$ to include the isotropic splittings of nuclei which lie in the plane of molecular framework, such as C^{13} or N^{14}. They found that the spin density and the hyperfine coupling constant for a C^{13} nucleus, which is joined to three other carbons, are related by the equation

$$A_C = Q_1\rho_0^\pi + Q_2(\rho_1^\pi + \rho_2^\pi + \rho_3^\pi) \qquad (2)$$

where ρ_0^π is the spin density on the C^{13} nucleus and ρ_1^π, ρ_2^π and ρ_3^π are the spin densities on the attached carbons. The Q's depend upon the ratio $J(\sigma\pi)/\Delta E$, where $J(\sigma\pi)$ is the exchange integral for the carbon sp² orbital with the π-orbital, and ΔE is the singlet–triplet separation of a C–C bond.

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(12) C. R. Smith, *J. Am. Chem. Soc.*, **46**, 414 (1924).

(13) F. C. Adam and S. I. Weissman, *ibid.*, **80**, 2057 (1958).

(14) E. de Boer and S. I. Weissman, *ibid.*, **80**, 4549 (1958).

(15) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

(16) A. D. McLachlan, H. H. Dearman and R. Lefebvre, *J. Chem. Phys.*, **33**, 65 (1960).

It should be noted that the values for the Q's quoted in the article by McLachlan, *et al.*, are in error.[17] Tuttle has also suggested a similar relationship for the spin densities at the carbon nuclei in naphthalene negative ion.[9]

To extend the work of McLachlan, *et al.*,[16] to a system such as the bipyridyl negative ion, it is necessary to discuss the contribution of the non-bonding pair of electrons to the values of the Q's in equation 2. The odd electron will polarize the non-bonding pair as it does the σ bonds. As a first approximation, the excited state of interest, for the nitrogen non-bonding electrons, is that resulting from an n-π transition.[18] The spin density at the nitrogen will therefore depend upon a term of the form $J(n\pi)/\Delta E_{n\rightarrow\pi}$, where $J(n\pi)$ is the exchange integral between the odd electron and the non-bonding pair, and $\Delta E_{n\rightarrow\pi}$ is the energy separation of the ground state of the non-bonding pair and the lowest π antibonding state. McLachlan[17] recently has shown, however, by symmetry considerations, that the exchange integral $J(n\pi)$ vanishes. It is possible that higher states of the non-bonding pair could contribute to the spin density at the nitrogen nucleus, but a comparison of the NH_2 nitrogen splitting with that of NH_3^+, recently observed by Cole,[19] indicates that the contribution of the non-bonding electrons to the nitrogen spin density is small.

We can estimate the spin densities of 4,4′-bipyridyl negative ion using the Hückel theory and then estimate values for the Q's in equation 2. The value of h used for the nitrogen coulomb integral is determined from the experimental ratios of the *meta* to *ortho* spin densities. This value of h is nearly zero. Therefore the spin densities of biphenyl negative ion should approximate those of bipyridyl negative ion. These values are $\rho_N = 0.159$, $\rho_o = 0.019$, $\rho_m = 0.089$ and $\rho_p = 0.123$, where ρ_N is the nitrogen spin density, ρ_o the *ortho* carbon spin density, etc. The measured values for ρ_o and ρ_m are 0.02 and 0.10, respectively. These values for the spin densities yield a value of $Q_1 = 19$ gauss and $Q_2 = 9.5$ gauss. It should therefore be possible to use the Hückel theory and these Q's to estimate the nitrogen coupling constants in other heterocyclic negative ions.

We have examined phenazine negative ion and have found a reasonable agreement between the observed spectrum and that calculated using the already known proton coupling constants for anthracene negative ion and a value for the nitrogen coupling constant of 3.2 gauss. Use of equation 2 and the Hückel spin density calculated for phenazine negative ion, assuming h equals zero, gives a value of 3.8 gauss for the nitrogen coupling constant. A more judiciously chosen value of h should improve the agreement. A value of 0.5 is suggested.

It therefore seems possible that the Hückel theory can be applied to heterocyclic negative ions, with the inclusion of equation 2, and an experimentally determined value of h for the nitrogen coulomb integral.

The values for the Q's for equation (2) were obtained by assuming $2Q_1 = Q_2$. The same sign for the Q's was chosen to agree with experimental results on the diazine negative ions (to be published). The relationship $2Q_1 = Q_2$, however, neglects the effect of exchange polarization of the nitrogen 1S and 2S electrons. This effect is small for the nitrogen atom, but may not be for heterocyclic nitrogens as indicated by Karplus and Fraenkel.[20] An estimation of the values of the Q's in equation (2) from a comparison of the experimental results of bipyridyl negative ion and pyrazine negative ion, without assuming a relation between Q_1 and Q_2, yields $Q_1 = 21.9$ gauss and $Q_2 = 5.8$ gauss.

Acknowledgments.—I wish to thank Dr. J. Swalen of Shell Development for his help in recording the spectrum in Fig. 1a and for the use of the Shell Development 100-kc. spectrometer. I am indebted to Dr. W. G. Schneider of the National Research Council for the sample of pyridine-2,6-d_2, and to helpful discussions with Professor A. Streitwieser and Dr. H. H. Dearman.

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(17) A. D. McLachlan, private communication.

(18) R. S. Mulliken, *J. Chem. Phys.*, **3**, 564 (1935).

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(20) M. Karplus and G. Fraenkel, *J. Chem. Phys.*, to be published.