Solutions of Alkali Metals in Anhydrous Pyridine

C. D. Schmulbach, C. C. Hinckley, and David Wasmund

Contribution from the Department of Chemistry, Southern Illinois University, Carbondale, Illinois 62901. *Received May 16, 1968*

Abstract: The dissolution of lithium, sodium, and cesium in pyridine gives first an unstable yellow solution which changes to an intense blue color. Frozen samples of the yellow lithium solutions give an epr signal. The paramagnetic species in the yellow solutions is presumed to be the pyridine radical anion, which at room temperature reacts rapidly to form almost exclusively the stable blue 4,4′-bipyridyl radical anion. A mechanism, which excludes hydrogen evolution and excess alkali metal, is proposed for the homogeneous reduction of pyridine to the 4,4′-bipyridyl radical by alkali metals. Ultraviolet spectra are reported for the pyridine radical anion and 4,4′-bipyridyl radical anion. An explanation is offered for the nearly exclusive formation of the 4,4′-bipyridyl radical anion.

We had observed that alkali metals dissolved in anhydrous pyridine gave an unstable yellow solution, which changed gradually in color to an intense blue. It had been shown in earlier studies that pyridine is reduced by potassium in anhydrous dimethoxyethane or tetrahydrofuran to give the blue 4,4′-bipyridyl radical anion.[1,2] When sodium was brought into contact with excess anhydrous pyridine at temperatures below 90° and the reaction mixture was oxidized, 4,4′-bipyridyl was obtained almost exclusively.[3] For temperatures above 90° and for increased reaction times, a mixture of bipyridyl isomers was formed.[3,4] Sodium reacts with anhydrous pyridine to give a reactive compound $Na\cdot 2C_5H_5N$,[5,6] which has no ammoniate counterpart.

The purpose of this research was to study the behavior of dilute solutions of alkali metals in pyridine under rigorous anhydrous and oxygen-free conditions and to characterize the solute species. The formulation of reasonable mechanisms to account for the observed color changes was sought in terms of identifiable solute species. Specifically, experiments were designed to determine whether an excess of alkali metal is necessary for the color change to occur, whether hydrogen gas is evolved during the color change, whether paramagnetic species exist in the yellow solution, and whether mixtures of bipyridyl isomers could be isolated from the blue solutions.

Results and Discussion

A yellow-brown material formed instantly on the surface of lithium metal when it was brought into contact with anhydrous pyridine. The yellow solid dissolved on shaking and the pale yellow solution which resulted was filtered of excess solid. The electronic spectrum of the yellow solution, which was obtained within 10 min after mixing, contained a single broad intense band at λ_{max} 330 mμ (ϵ 9 × 10^3) shown in Figure 1. A band at λ_{max} 335 mμ (ϵ 2000) was reported for a solution of sodium and pyridine in anhydrous tetrahydrofuran.[7] The yellow pyridine solution gradually changed in color to green and finally to blue. It is significant that the color changes in the solution occur in the absence of solid (excess) alkali metal.

The electronic spectrum of the blue solution contained two bands at λ_{max} 381 mμ (apparent ϵ 3 × 10^4–9 × 10^4)[8] and at 570 mμ (apparent ϵ 9 × 10^3–3 × 10^4). The electronic spectrum of a blue solution of sodium is identical with that of lithium with two intense bands at 381 mμ (ϵ 3 × 10^4–9 × 10^4) and 570 mμ (ϵ 8 × 10^3–2 × 10^4). The spectrum of the blue cesium–pyridine solution contains the same two bands.

The blue solutions of sodium and of lithium in anhydrous pyridine both gave an epr spectrum identical with that reported for the 4,4′-bipyridyl radical anion.[1] The combined spectral and epr data leave no doubt that the solute species responsible for the blue coloration is either the 4,4′-bipyridyl radical anion or the $[M^+,C_{10}H_8N_2\cdot^-]$ ion pair or a combination of the two. The low dielectric constant of pyridine (ϵ 12.3) requires the consideration of ion pairs in data interpretation.

Yellow solutions of lithium at room temperature were examined within 8 min of mixing by epr spectroscopy. No signal was observed. After 15 min, a weak signal appeared which finally developed into the characteristic pattern for the 4,4′-bipyridyl radical. On the assumption that the failure to observe an epr signal in the liquid sample was due to severe signal-broadening strong relaxation processes of unknown origin, the yellow solutions were frozen to liquid nitrogen temperatures within 9 min of mixing and epr spectra taken. The frozen samples exhibited a single signal at $g = 2.002$. The spectrum had a width of 22 G and no hyperfine structure was observed. We propose that the paramagnetic species is the $C_5H_5N\cdot^-$ radical anion.

A reasonable assignment of the electronic absorption band at 330 mμ to a $\pi^* \rightarrow \pi^*$ ($^2A_2 \leftarrow {}^2B_1$) transition in the $C_5H_5N\cdot^-$ radical can be made. It had been observed previously that solutions of 10^{-3}–10^{-4} *M* sodium and pyridine in anhydrous tetrahydrofuran gave two bands in the ultraviolet spectrum at 335 mμ (ϵ 2000) and at 244 mμ (ϵ 3340), which were attributed to a $C_5H_5N\cdot^-$ radical anion.[7] These solutions, like our pyridine solutions, lost this characteristic spectrum "moderately rapidly." The 244-mμ band we assign

---

[1] A. Carrington and J. Santos-Veiga, *Mol. Phys.*, **5**, 21 (1962).

[2] R. L. Ward, *J. Amer. Chem. Soc.*, **83**, 3623 (1961).

[3] C. R. Smith, *ibid.*, **46**, 414 (1924).

[4] R. Setton, *C. R. Acad. Sci., Paris, Ser. A.B*, **244**, 1205 (1957).

[5] B. Emmert, *Chem. Ber.*, **47**, 2598 (1914); **49**, 1060 (1916).

[6] B. Emmert and P. Buchert, *ibid.*, **54**, 204 (1921).

[7] J. W. Dodd, F. J. Hopton, and N. S. Hush, *Proc. Chem. Soc.*, 61 (1962).

[8] The solubility in pyridine of the metal hydride which is formed in the reaction is unknown. The values of the extinction coefficients are based on the limiting cases for $3M + 2C_5H_5N = M^+,(C_5H_4N)_2^- + 2MH$ in which the hydride is totally insoluble or completely soluble, respectively.

to the $\pi \rightarrow \pi^*$ ($^2A_2 \leftarrow {}^2B_1$) transition since the corresponding π–π^* ($^1B_2 \leftarrow {}^1A_1$) transition in pyridine appears around 250 mμ with an extinction coefficient ranging from 2000 to 5000 depending upon the solvent.[9] The $\pi \rightarrow \pi^*$ transition was not observed in the lithium–pyridine system due to the strong solvent absorption below 300 mμ. The possibility that the absorption band at 330 mμ is due to a $n \rightarrow \pi^*$ transition is rejected because this band would be found near 250 mμ.[9]

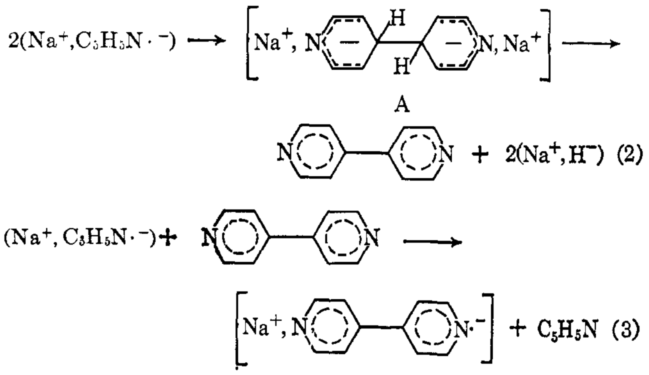
To test the possibility that the 4,4′-bipyridyl radical anion is formed according to the reaction

$$M + 2C_5H_5N = (M^+, C_{10}H_8N_2\cdot^-) + H_2$$

careful measurements of gas evolution were undertaken. These studies showed that during the period of color change from yellow to blue there is no increase in pressure in a sealed apparatus containing lithium or sodium and pyridine. Sufficient amounts of alkali metal were used to produce a hydrogen pressure of 1 atm if the reaction occurred as described above. Upon cooling the blue solution to its freezing point, no gas was evolved. This indicates that no hydrogen gas was dissolved in the pyridine. The possibility that any hydrogen gas first formed reacted with pyridine or bipyridyl was eliminated by a vpc analysis of the blue solutions which had been discolored by opening the sealed apparatus to the atmosphere. Only 4,4′-bipyridyl (99.4 mol %) and 2,2′-bipyridyl (0.6 mol %) were present. No piperidine or reduced bipyridyls were detected. It was concluded that no reaction involving hydrogen as a product could be used to account for the formation of the 4,4′-bipyridyl radical.

In developing a mechanism to account for the formation of the bipyridyl radical, the following factors were considered. (1) A reactive paramagnetic species is formed initially when an alkali metal is dissolved in anhydrous pyridine. (2) The formation of the 4,4′-bipyridyl radical occurs in the yellow 10^{-4} *M* metal solutions which have been filtered of excess solid metal. (3) The 4,4′-bipyridyl radical is formed almost exclusively as the reaction product. The most reasonable mechanism which conforms to these conditions is shown in eq 1–3. The species A may be viewed either as an activated complex or as a reactive intermediate without destroying the mechanistic hypothesis. The apparent irreversibility of the reaction may be attributed to greater stability of the 4,4′-bipyridyl radical relative to the pyridine radical anion. A mechanism, recently proposed, for the formation of the 4,4′-bipyridyl radical in the presence of solid alkali metal is inappropriate to our homogeneous systems.[10]

$$3Na + 3C_5H_5N \longrightarrow 3(Na^+, C_5H_5N\cdot^-) \quad (1)$$



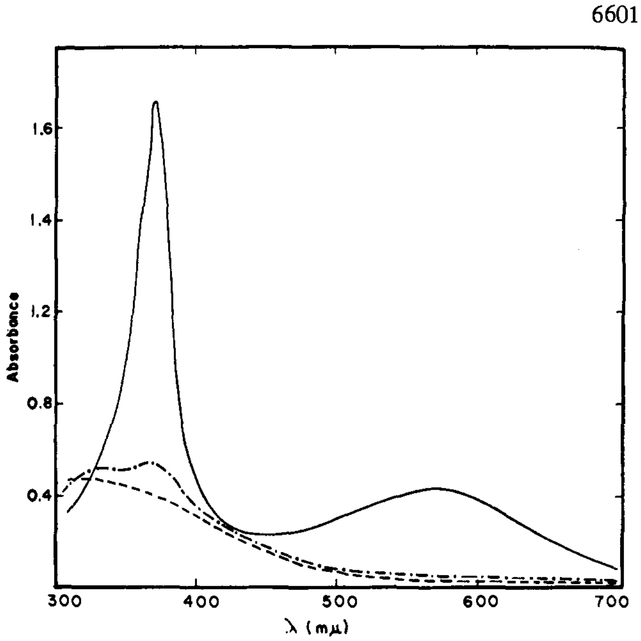


Figure 1. Electronic spectra of solution of lithium in pyridine at room temperature. Spectrum of yellow solution taken within 10 min of mixing (- - - - - -); spectrum after 23 min (–·–·–·–·–); spectrum of stable blue solution taken after 72 hr (——).

In order to further test the validity of our mechanism and to provide experimental evidence in support of the hypothesis that the instability of the pyridine radical anion stems from the lability of the hydrogen in the 4 position, spectral and epr studies were repeated on solutions of lithium in 4-methylpyridine (γ-picoline). The electronic spectrum of a yellow solution of lithium in γ-picoline, taken within 7 min after mixing, showed a single band at 331 mμ (ε 6 × 10^3). The solution retained the yellow color and after 5 days the position and intensity of the band remained fixed at 326 mμ (7 × 10^3). A very small impurity of less than 0.3 mol % was detected by vpc in the γ-picoline used in these experiments. This impurity could not be removed by normal purification procedures and was presumed to be β-picoline, an isomer which has a boiling point very near that of γ-picoline. The epr spectra of the yellow solutions, taken at room temperature within 7 min of mixing, showed a single broad (~15 G) signal without hyperfine structure at $g = 2.002$. After 12 min a signal began to develop with a somewhat higher g factor having hyperfine splitting of about 0.6 G, continued to increase for several hours, and then remained unchanged. Although the second signal overlapped the first, both signals were distinguishable. Comparison of the spectrum with those obtained earlier in the research from solutions prepared from less carefully purified γ-picoline suggests that the signal with hyperfine structure is a radical formed by condensation of the solvent impurity. We propose that the broad signal is due to the γ-picoline radical anion. The data indicate that the methyl group in the 4 position effectively blocks the rapid decomposition of this radical.

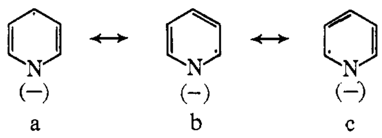
---

[9] See H. J. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, Chapter 14.

[10] A. A. Ziyaev, O. S. Otreshchenko, V. B. Leont'ev, and A. S. Sadykov, *J. Org. Chem.* (USSR), 3, 1918 (1967).

Perhaps the most striking feature of the chemical reaction of an alkali metal with pyridine is the remarkable degree of chemical selectivity which gives almost exclusively the 4,4′ isomer. We propose that the unpaired electron density on the pyridine radical anion affects the choice of reaction site and further, that this density on the 4-carbon is great enough to dominate the course of the reaction. Both molecular orbital and valence bond models lend support to these conclusions. An MO model of the pyridine radical is represented most simply as a pyridine molecule with an additional electron added to the lowest lying π^* orbital. The calculations of Mataga and Nishimoto[11] show that, for the lowest π^* orbital of pyridine, the maximum electron density is on the 4-carbon. This result is only indicative, however, since there is substantial electron density on the 2,6- and 3,5-carbons as well. An MO calculation for the pyridine radical would be more useful.

The valence bond model leads substantially to the same conclusions. Of the many canonical structures that are possible for the pyridine radical, the structures



which place the negative charge on the highly electronegative nitrogen atom, should be more important. Of these, structure a provides the greatest separation between the negative charge and the unpaired electron and should, therefore, make the greatest contribution to the total structure. It should be noted that no resonance structures may be drawn which place the negative charge on the nitrogen *and* the unpaired electron at a 3- or 5-carbon. Additionally, though it is not required, the valence bond model suggests a change in hybridization of the atom with the greatest unpaired electron density.

Experimental Section

Reagents. Pyridine (Fisher reagent) and γ-picoline (Aldrich, 98%) were purified by distillation from KOH pellets. The center fractions were collected and stored over molecular sieves (Linde 4A). Final dehydration was accomplished by distilling the amines from sodium into a closed dry apparatus on a vacuum line.

Lithium rod (Lithium Corp. of America) was cut in an atmosphere of dry argon and sealed *in vacuo* behind bulb-type break-seals. Sodium (MCB) was distilled *in vacuo* into ampoules fitted with break-seals or directly into the reactions vessels attached to the vacuum line. Cesium was prepared by heating a mixture of cesium chloride (Fisher certified) and calcium turnings *in vacuo*. The cesium metal was distilled directly into the reaction vessel.

General Procedure. Standard high-vacuum line techniques were used. For the hydrogen pressure experiments a clean piece of sodium or lithium was placed in an apparatus of known volume which had been sealed to the vacuum line. The apparatus consisted of a 50-ml flask connected to a mercury manometer that could measure pressure changes as small as 1 mm. Dry pyridine was condensed into the apparatus and the apparatus was sealed from the vacuum line. No pressure change was observed for a period of 2 months.

Spectral Measurements. Visible-ultraviolet spectra were recorded on a Beckman DK-1A spectrometer. At no time were the solutions open to the atmosphere.

The epr spectra were obtained with a Varian V4502-15 epr spectrometer.

Analysis. The concentrations of the metal ions were determined by Galbraith Laboratories, Knoxville, Tenn., by atomic absorption spectrometry.

Acknowledgment. The authors wish to thank the National Science Foundation for providing funds for the epr spectrometer.

---

[11] N. Mataga and K. Nishimoto, *Z. Phys. Chem.* (Frankfurt am Main), **13**, 140 (1957).

The Crystal Structure of the Tetrachloroaluminate Salt of the Heptamethylbenzene Cation[1a]

N. C. Baenziger and A. Dwayne Nelson

Contribution from the Department of Chemistry, University of Iowa,
Iowa City, Iowa. Received April 27, 1968

Abstract: The crystal structure of the tetrachloroaluminate salt of heptamethylbenzene, $[(CH_3)_7C_6]^+[AlCl_4]^-$, was determined from single-crystal X-ray diffraction data (film method, visual estimates, 1900 reflections). The monoclinic unit cell data are $a = 8.641 \pm 3$, $b = 12.581 \pm 3$, $c = 16.51 \pm 1$ Å, $\beta = 94.35 \pm 7°$, $P2_1/n$, $D_x = 1.26$ g/cm^2. The structure was refined by least-squares methods to $R_1 = 0.090$. The $AlCl_4^-$ anion exists as a nearly perfect tetrahedron with an average Al–Cl bond length of 2.120 ± 0.004 Å and an average Cl–Cl length of 3.462 ± 0.004 Å. The cation consists of a seventh methyl group σ-bonded to hexamethylbenzene forming a *gem*-dimethyl group. The cation has idealized point group symmetry C_{2v} with two nearly perpendicular planes containing all of the carbon atoms. A simple (HMO) calculation was performed on the five sp^2-bonded ring carbon atoms, and the calculated bond orders are in agreement with the observed bond distances.

The catalyst in reactions of the Friedel–Crafts type often become inactive after a relatively short time. In the methylation of benzene and its methyl homologs with methyl chloride and aluminum trichloride at 80°, deactivation sets in rapidly with the consumption of relatively large quantities of catalyst.[1b] The nmr[1b] spectrum of the heptamethylbenzene cation is con-

---

[1] (a) This work was supported by National Science Foundation Grant GP-6855. (b) W. von E. Doering, M. Saunders, *et al.*, *Tetrahedron*, **4**, 178 (1958).