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Electron Spin Resonance Study of 1-Hydropyridinyl Radicals in Solution. 4-Acetylpyridine and Pyridine-4-carbaldehyde

JÜRGEN K. DOHRMANN AND WOLFGANG KIESLICH

Institut für Physikalische Chemie und Quantenchemie der Freien Universität Berlin, Fabeckstrasse 32, D-1000 Berlin 33, Germany

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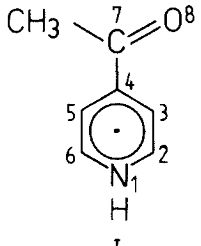
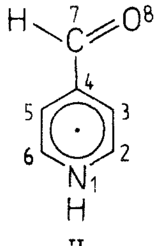
The electron spin resonance spectra of the transient 1-hydropyridinyl radicals produced by the photochemical reduction at room temperature of 4-acetylpyridine and pyridine-4-carbaldehyde in 2-propanol/acetone solution with a range of water content have been analyzed. The NH proton couplings were assigned by investigating the spectra of the radicals in solutions containing D_2O. An effect of the solvent on the hyperfine couplings has been observed. The solvent effect has been treated by the Hückel–McLachlan procedure assuming that the Coulomb-integral parameter of the carbonyl oxygen atom is changed by the solvent. The result of the calculation is in agreement with the observation and leads to an assignment of the couplings.

INTRODUCTION

We have reported ESR studies (*1*, *2*) of some substituted 1-hydropyridinyl radicals generated by the photoreduction of substituted pyridines in a solvent mixture of 2-propanol and acetone. We now communicate a solvent effect on the ESR spectra of the transient radicals **I** and **II** seen during the photolysis of 4-acetylpyridine and pyridine-4-carbaldehyde in 2-propanol/acetone solutions with a range of water content. The solvent effect is rationalized in terms of the Hückel–McLachlan MO model. On the basis of the MO model and the exchange of the NH proton by the deuteron in the presence of D_2O, we suggest an assignment of the ring proton couplings in the radicals. The ESR parameters of radical **II** in the absence of water and a tentative assignment of the couplings have previously been reported (*2*).



I



II

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EXPERIMENTAL

The radicals were generated by *in situ* photolysis (*3*). Details have been described elsewhere (*1*, *2*). The solutions of 4-acetylpyridine (EGA–Chemie) and pyridine-4-carbaldehyde (Merck–Schuchardt) in a solvent made up of equal parts by volume of 2-propanol and acetone contained up to 50% by volume of H_2O or D_2O. They were freed of dissolved oxygen by purging with pure nitrogen and were photolyzed at 22 to 24°C while they slowly flowed through the flat sample cell. The unfiltered light of a high-pressure mercury lamp (Philips SP 500 W) was used. The pyridine-4-aldehyde was distilled *in vacuo* under nitrogen. The 4-acetylpyridine was used as supplied.

The ESR spectra were taken with a Varian E-9 spectrometer at about 9.5 GHz and employing 100-kHz-field modulation. For computer analysis of the hyperfine structure, the spectra were digitized by a Nicolet 1074 computer of average transients (CAT) equipped with a paper tape punch. The magnetic field was scanned by the field-frequency lock unit E-272 B which was controlled by the sweep output voltage of the CAT. The 4096 memory addresses of the CAT were advanced by the step motor pulses from the pen recorder of the spectrometer. The memory addresses were calibrated in units of magnetic field by means of a proton NMR gaussmeter. The NMR probe correction was determined using the g value of the 1-hydropyridinyl radical (*4*) as a reference standard. The microwave and NMR signal frequencies were measured with an electronic counter (Hewlett–Packard 5245 L equipped with the heterodyne converter HP 5255 A).

The analysis of the hyperfine structure and the determination of the couplings and the values of g were performed by use of a computer program developed in this laboratory (*5*). The procedure has been outlined elsewhere (*6*). The estimated accuracy of the couplings and g values is better than 20 mG and 4×10^{-5}, respectively. The experimental and simulated spectra shown in this work are graphs prepared by the computer.

RESULTS AND DISCUSSION

The low-field half of the spectrum of 1-hydro-4-acetylpyridinyl (**I**) recorded during the photolysis at 24°C of a 0.03 *M* solution of 4-acetylpyridine in 2-propanol/acetone (equal parts by volume) is shown in Fig. 1. The high-field portion of the spectrum was slightly less intense. Radical **I** is short-lived. The signal immediately disappeared when the photolysis was interrupted. Spectra of radical **I** were also taken during the photolysis of 0.1 *M* solutions of 4-acetylpyridine with up to 50% by volume of water (Fig. 2). Strong solvent-induced shifts in the couplings are obvious from the comparison of the outermost portions of the spectra. A further increase of the water content was prevented by the precipitation of photolysis products.

The spectrum of 1-hydropyridinyl-4-carbaldehyde (**II**) in the absence of water has been reported previously (*2*). The spectra obtained in the presence of water were generally weaker. Figure 3 shows the low-field half of the spectrum from radical **II** present during the photolysis at 24°C of a 0.1 *M* solution of pyridine-4-carbaldehyde in 2-propanol/acetone (equal parts by volume) with 11.8% by volume of water. With still larger concentrations of water the spectra became too weak.

The ESR parameters of the radicals are listed in Table 1. The coupling of the NH proton, a_1^H, was assigned experimentally by generating the radicals in solutions

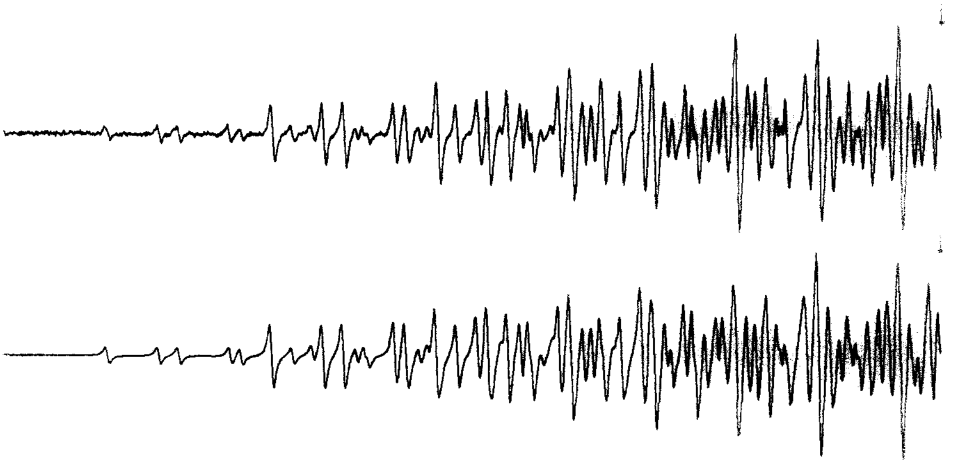

FIG. 1. Low-field half of the experimental spectrum (top) of the 1-hydro-4-acetylpyridinyl radical in 2-propanol/acetone (1 : 1 by volume) and simulated half-spectrum (bottom). The field scan is 18 G.

containing D_2O. With 50% by volume of D_2O the exchange of the NH proton of radical **I** was complete. The measured deuteron coupling of 0.80 G was a little larger than the value of 0.77 G expected for the exchange of the proton with the coupling of 5.03 G. With 11.8% by volume of D_2O both isotopic forms of radical **II** were observed. A reasonably satisfactory simulation was obtained for a ratio of 1 : 2 for the protonated and deuterated forms and couplings of 4.62 and 0.80 G for the nitrogen and the deuteron, respectively, in the deuterated form of radical **II**. Since the temperature dependence of the couplings has not been investigated, it is not clear whether the small shifts in the couplings observed upon deuteration indicate the contribution of vibronic motion. The assignment of the CH proton couplings is discussed below. As expected,

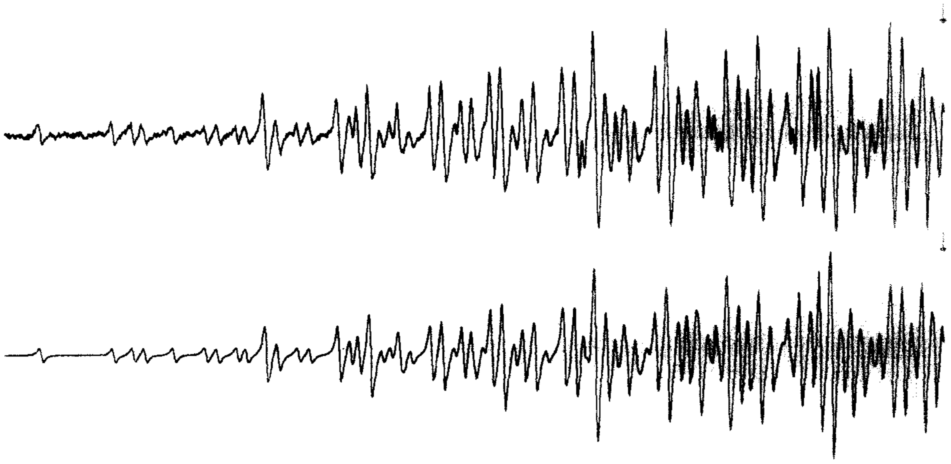

FIG. 2. Low-field half of the experimental spectrum (top) of the 1-hydro-4-acetylpyridinyl radical in 2-propanol/acetone (1 : 1 by volume) with 50% by volume of water and simulated half-spectrum (bottom). The field scan is 18.5 G.

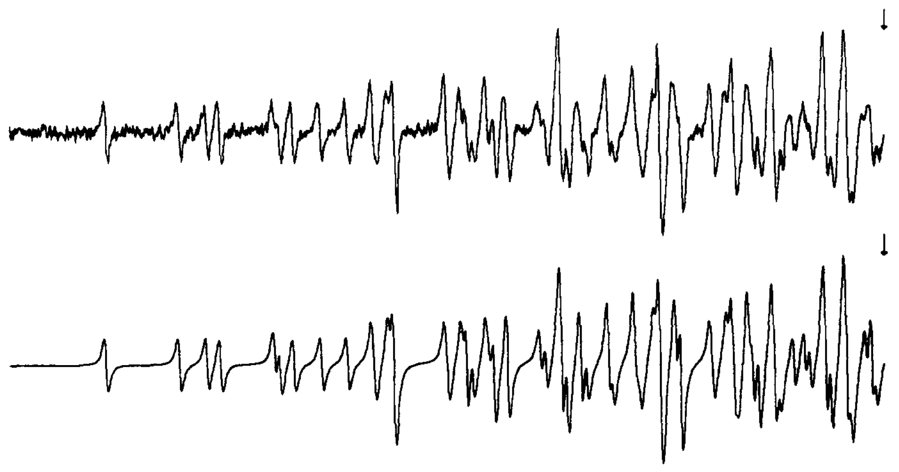

FIG. 3. Low-field half of the experimental spectrum (top) of the 1-hydropyridinyl-4-carbaldehyde radical in 2-propanol/acetone (1 : 1 by volume) with 11.8% by volume of water and simulated half-spectrum (bottom). The field scan is 15.4 G.

TABLE 1

HYPERFINE COUPLINGS[a] (ABSOLUTE VALUES[b] IN GAUSS) AND g VALUES[b] OF THE 1-HYDRO-4-ACETYLPYRIDINYL (I) AND 1-HYDROPYRIDINYL-4-CARBALDEHYDE (II) RADICALS AT 24°C IN 2-PROPANOL/ACETONE (EQUAL PARTS BY VOLUME) WITH A RANGE OF WATER CONTENT

Radical	H_2O (vol%)	g	a_1^{N}	a_1^{H}[c]	a_2^{H}	a_3^{H}	a_5^{H}	a_6^{H}	$a_{\mathrm{R}}^{\mathrm{H}}$
I	—	2.00370	4.77	4.99	3.16	0.99	1.37	2.56	3.14[d]
	11.8	2.00364	4.71	5.03	2.94	1.17	1.55	2.35	3.61[d]
	30.0	2.00361	4.70	5.06	2.76	1.33	1.69	2.18	4.05[d]
	50.0	2.00359	4.63	5.03	2.60	1.42	1.80	2.03	4.40[d]
II	—[e]	2.00379	4.71	5.03	3.14	1.13	1.84	1.93	4.62[f]
	11.8	2.00380	4.68	5.05	2.96	1.29	2.01	1.77	5.05[f]

[a] For assignment, see text.

[b] Estimated errors are ±20 mG and $\pm 4 \times 10^{-5}$ for the couplings and the g value, respectively.

[c] NH proton coupling as assigned by deuterium exchange.

[d] CH_3 proton coupling.

[e] See also Ref. (*2*).

[f] CHO proton coupling.

the nitrogen and ring coupling constants of radical I are similar to those of radical II. The methyl proton coupling replaces the largest CH proton coupling of radical II. This is consistent with the result of the MO calculation of the π-spin population for radical II (*2*). From the absence of pairs of equivalent protons in radical I it is deduced that the rotation of the acetyl group is strongly hindered. This parallels the findings for the anion of radical I (*7*) and for the formyl group of radical II.

Inspection of Table 1 shows that, except for the couplings of the nitrogen and the NH proton, all couplings and the value of g are sensitive to the addition of water. In radical

I, the couplings of the methyl protons and of the protons to be assigned to the 3- and 5-positions (see below) increase by about 40%, while those of the two remaining protons decrease by about 20% with increasing concentration of water. The same solvent effect is observed for radical **II**. A similar, although much stronger, effect of the solvent on the couplings of the 1-methyl-4-acetylpyridinyl radical was recently reported and was explained in terms of different contributions from polar and nonpolar resonance structures to the distribution of spin density (*8*). This model, however, did not explain why the nitrogen and the N–CH_3 proton couplings were nearly independent of the polarity of the solvent.

It has been shown that the Hückel–McLachlan π–MO model (*9*) can account for the solvent dependence of the hyperfine splittings in semiquinone radical anions, if it is assumed that the solvent affects the electronegativity of the oxygen atom (*10*). Changes in the electronegativity were simulated by proper adjustment of the Coulomb-integral parameter. The solvent effect observed for radicals **I** and **II** can be rationalized by similar arguments. The strongest solvent-dependent interactions are expected between the oxygen atom of the radicals and the hydrogen-bond-forming molecules of the solvent mixture. Figure 4a presents the McLachlan π-spin population in radical **I** as a function of the Coulomb-integral parameter h_0 of the oxygen atom. A constant value of 1.6 was used for the resonance-integral parameter of the carbon–oxygen bond. As in previous work (*1*, *2*), a value of 1.0 was chosen for the Coulomb-integral parameter of the nitrogen atom. The Coulomb-integral parameter for the carbon atom in position 3 was –0.07. This allowed for the inductive effect of the adjacent oxygen in the planar radical and reproduced the observed inequivalence of the ring proton couplings. The hyperconjugation model was chosen for the methyl group, and the parameters were taken from the literature (*11*). The parameter λ in the McLachlan calculation was kept fixed at 1.2. The comparison of the calculated McLachlan spin population (Fig. 4a) and the plot (Fig. 4b) of the solvent dependence of the couplings in radical **I** shows that the model reproduces both the direction and order of magnitude of the observed variation in the proton couplings and substantiates the assignment given in Table 1. It may therefore be concluded that the solvent effect is due to the redistribution of the π-spin

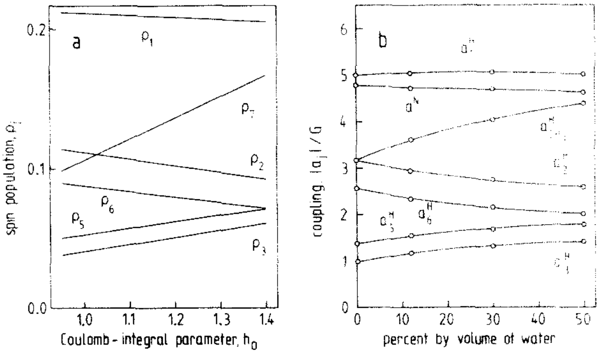

FIG. 4. Calculated McLachlan π-spin population for 1-hydro-4-acetylpyridinyl as a function of the Coulomb-integral parameter of the oxygen atom (a) and dependence of the couplings (absolute values) on the water content of the solution (b).

population induced by the interaction between the carbonyl oxygen atom of the radical and the water molecule. It is reasonable to assume that the formation of a larger fraction of radicals with hydrogen bonds between the oxygen atom and the water molecule requires an increase in the Coulomb-integral parameter h_0. Values of h_0 of 0.95 and of 1.4 for the radical in solutions without and with 50% by volume of water, respectively, result in a good agreement between experimental and calculated π-spin populations on the ring carbon atoms. The experimental spin population was determined by use of the McConnell parameter $Q^{\mathrm{H}}_{\mathrm{CH}} = -27.7 \pm 1.1$ G (*1*) and assuming a negative sign of the ring proton couplings. The calculated spin population on the nitrogen atom is least affected by the value of h_0. This is also in accord with the observation. From the NH proton coupling taken with a negative sign and the calculated spin population on the nitrogen atom, a value of −24 G is deduced for the McConnell parameter $Q^{\mathrm{H}}_{\mathrm{NH}}$. This is another example for the observation (*2*) that 1-hydropyridinyl radicals substituted by electron-withdrawing groups in the 4-position require a larger absolute value of $Q^{\mathrm{H}}_{\mathrm{NH}}$ than that derived from the 1-hydropicolinyl radicals (*1*).

The solvent effect observed for radical **II** can be explained in a completely analogous manner. The model leads to the assignment given in Table 1.

ACKNOWLEDGMENT

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