STRUCTURES OF 2-HYDROXYPYRIDINE AND ITS VINYL DERIVATIVES

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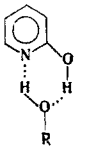
The PMR, Raman, and UV absorption spectra of 2-hydroxypyridine and its vinyl derivatives were investigated. Their electrochemical reduction was studied, and a quantum-chemical analysis of them was performed. It was concluded that the structure of 2-hydroxypyridine in proton-donor solvents is mesomeric, and its wave function, to a first approximation, is a linear combination of the wave functions of the 2-pyridone and zwitterion models. The contribution of the wave functions of each of the models depends substantially on the concentration of the solution and the nature of the solvent. An assumption was made regarding the presence of dynamic conjugation between the vinyl group and the ring in vinyl derivatives of 2-hydroxypyridine.

Many years of investigation of the tautomeric transformations of 2-hydroxypyridine (2-HP) have made it possible to obtain considerable information regarding its structure and physicochemical properties [1-4]. It has been established that 2-HP has the 2-pyridone structure in inert solvents. The problem of the properties of this compound in strongly acidic and strongly alkaline media is more or less clear. The greatest difficulties are encountered in attempts to unambiguously explain the results obtained during a study of 2-HP in weakly acidic, weakly alkaline, and neutral aqueous and alcohol solutions. In recent years, the hypothesis of the existence of the molecule in the form of a zwitterion under these conditions has often been used. However, it must be taken into account that the resonance formulas of 2-hydroxypyridine, 2-pyridone, and the zwitterion, as well as the position of the hydrogen atom, differ only with respect to the distribution of the π electrons and the character of the hybridization of the AO of nitrogen. When this is taken into account, the mesomeric form may prove to be preferable. This should be facilitated by the hydrogen bonds that develop in aqueous and alcohol solutions; the stability of these hydrogen bonds may increase additionally as a result of the formation of quasiaromatic rings similar to the naphthalene ring.

It is easy to see that the I-II and III-IV models may prove to be resonance models and may give several intermediate structures. In this case, a number of the observed properties will be found to be in agreement with the hypothesis of a lactim–lactam tautomerism.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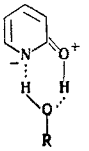
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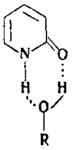
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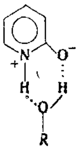
IV

In a previous paper [5], we reported new results regarding the reactivity of 2-HP and its spectral characteristics. In the present investigation, we have continued our physicochemical study of this mole-

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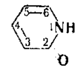
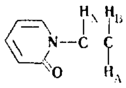
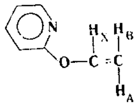
Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 95-102 January, 1972. Original article submitted May 28, 1970.

TABLE 1. Results of the Measurement of the PMR Spectra of 2-HP and Its Vinyl Derivatives

Compound	Solvent	Chemical shifts, δ, ppm						
		3-H	4-H	5-H	6-H	H_A	H_B	H_X
	Dioxane	6,42	7,18—7,43	6,11	7,18—7,43			
	$CHCl_3$	6,51	7,27—7,50	6,20	7,27—7,50			
	CD_3OD	6,51	7,33—7,66	6,35	7,33—7,66			
	H_2O—1*	6,67		6,45				
	H_2O—2	6,55	7,36—7,75	6,45	7,36—7,75			
	H_2O—3	6,53	7,36—7,76	6,49	7,36—7,76			
	CCl_4	6,35	7,27	6,08	7,62	5,32	4,89	7,39
	CCl_4	6,70	7,43	6,70	8,03	4,78	4,38	7,67

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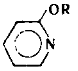
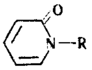
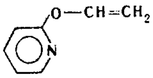
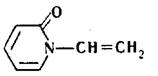
*The numbers 1, 2, and 3 correspond to different 2-HP concentrations (1 > 2 > 3). The range of change was from ~ 10 to 0.2 mole %.

TABLE 2. Results of the Calculation of the First Electronic Transitions in the Investigated Molecules

Compound (R = H, Alk)	Parameters of the electron transitions (λ is the wavelength, nm; *f* is the oscillator strength)			
	λ_1 (f_1)	λ_2 (f_2)	λ_3 (f_3)	λ_4 (f_4)
	266 (0,09)	218 (0,25)	182 (0,89)	180 (0,91)
	280 (0,32)	234 (0,12)	191 (0,59)	183 (0,10)
	268 (0,12)	226 (0,42)	192 (0,059)	186 (0,32)
	291 (0,33)	240 (0,09)	212 (0,26)	207 (0,07)

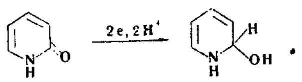
cule. A quantum-mechanical calculation of 2-HP models was performed, the PMR spectra were measured in greater detail, and the polarographic reduction was studied. The latter was carried out with a background of 0.1 M $(C_4H_9)_4NBr$ in 20% aqueous alcohol at various temperatures and heights of the mercury column and also on a background of a similar 0.05 M solution of $(C_4H_9)_4NOH$. The polarogram corresponds to Eq. (1), in which the reciprocal slope is 88 mV ($E_{1/2}$ = − 2.191 V).

$$E=E_{1/2}-\frac{RT}{\alpha nF}\ln\frac{i}{i_{lim}-i} \tag{1}$$

The elevated reciprocal slope is evidence for the irreversible nature of the reduction. The average temperature coefficient (3.44% per degree) only slightly increases the theoretical value for the diffusion current (2% per degree). The dependence of the limiting current on the height of the mercury column satisfies the equation

$$i_{lim}=k\sqrt{H_{Hg}}. \tag{2}$$

Thus, the scheme for the reduction of 2-HP can be represented as



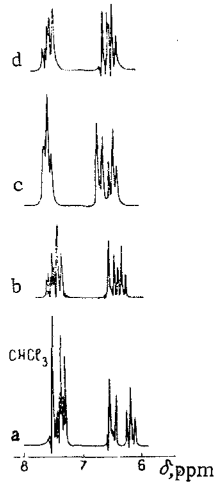


Fig. 1

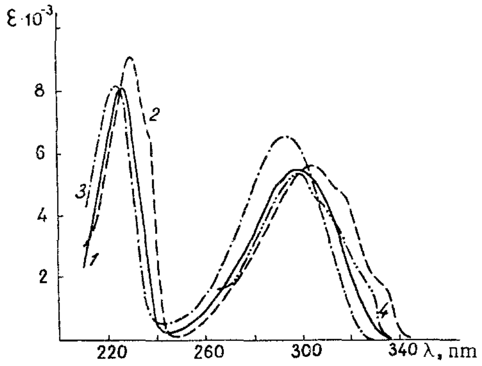


Fig. 2

Fig. 1. PMR Spectra of 2-HP in $CHCl_3$ (a), CD_3OD (b), H_2O-1 (c), and H_2O-3 (d).

Fig. 2. UV spectra of 2-HP in alcohol (1), dioxane (2), water at pH 7 (3), and benzene (4).

The limiting reduction current decreases somewhat ($E_{1/2} = -2.240$ V) on a 0.05 M $(C_4H_9)_4NOH$ background. The polarogram corresponds to Eq. (1), in which the reciprocal slope, as before, is elevated, which is also evidence for the irreversible character of the reduction. Under these conditions, the average temperature coefficient is already ~6.5% per degree, which indicates the kinetic limitations of the electroreduction. Equation (2) is not observed in this case. On the basis of the above, it can be concluded that an equilibrium state exists between the polarographically active and inactive forms of the depolarizer during the reduction of 2-HP on a $(C_4H_9)_4NOH$ background. The polarographically active form is probably the same as during the reduction on the $(C_4H_9)_4NBr$ background, while the nonactive form is the 2-HP anion, as proposed on the basis of a study of the UV spectra [5].

Proton magnetic resonance spectroscopy was used to investigate 2-HP in various solvents. In view of the fact that the 2-hydroxypyridine and 2-pyridone structures have different ring π-electron systems, the chemical shifts of their protons should differ. In addition, 2-pyridone has a carbonyl group, the magnetic anisotropy of which should affect the position of the signals.

Resonance between structures I-IV or tautomerism between the corresponding compounds should lead to PMR spectra with an averaged character.

The use of formula (3) may give approximate information regarding the shift of the A $\rightleftarrows$ B tautomeric equilibrium (A and B are the compounds that have pyridone and pyridine rings, respectively) or regarding the character of the mesomeric structure.

$$x_B = \frac{\delta_A - \delta_{obs}}{\delta_A - \delta_B} \qquad (3)$$

In formula (3), x_B is the mole fraction of model B or its contribution to the mesomeric structure, and δ are the chemical shifts.

It is apparent that structures I-IV should be taken into account in the discussion, but to somewhat simplify the problem, we will examine the shift from the pyridone to the pyridine ring. The results of a measurement of the PMR spectra of 2-HP in dioxane, chloroform, deuterated methanol, and water are presented in Table 1. The spectra were recorded with a JNM-4H-100 spectrometer at room temperature. Hexamethyldisiloxane was used as the internal standard. The chemical shifts are presented on the δ scale. The signal of the 5-H proton appears as a triplet caused by spin–spin coupling with 4-H and 6-H with the same constant J = 6 Hz. The 3-H signal is a doublet caused by spin–spin coupling with 4-H (J = 10 Hz). The 4-H and 6-H signals give a weak-field multiplet.

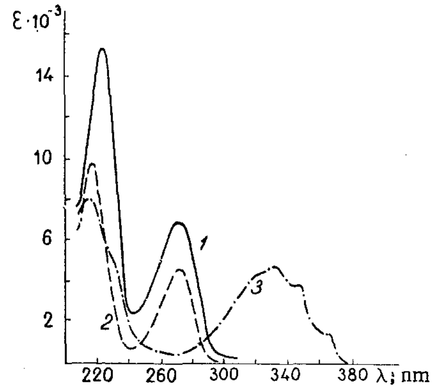


Fig. 3. UV spectra of 2-vinyloxypyridine (1), 2-ethoxypyridine (2), and 1-vinyl-2-pyridone (3) in cyclohexane.

A characteristic feature in the spectrum of 2-HP is a shift in the ring proton signals to weak field on passing from dioxane solutions to chloroform, deuterated methanol, and water solutions. Chloroform shifts all of the lines by 0.09 ppm. When chloroform is replaced by CD_3OD, the 5-H signal is shifted by another 0.15 ppm, and the 3-H signal does not change position. In water, the position of the signal depends on the concentration. As the concentration decreases, the 3-H signal goes to strong field, and the 5-H signal goes to weak field, and they thereby approach one another. As a result, a multiplet is observed instead of the distinctly separated triplet and doublet (Fig. 1). The 4-H and 6-H signals are also shifted differently; the spectral region occupied by them increases by 0.15 ppm.

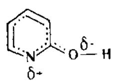
For comparison, we present the chemical shifts in 1-methyl-2-pyridone, in which the 3-H, 4-H, 5-H, and 6-H signals are found at 6.57, 7.26, 6.15, and 7.31 ppm, respectively. The 3-H and 5-H positions in the spectrum of pyridine coincide, while the 4-H and 6-H positions differ by 1.14 ppm (7.36 and 8.50 ppm).

Considering these data, it can be concluded that the structure of 2-HP in dioxane and chloroform is either close to pyridine, or that this molecule exists for most of the time as 2-pyridone.

Using formula (3), the data for 1-methyl-2-pyridone and pyridines, and roughly taking into account the effect of the methyl and hydroxyl groups, we found that the contribution of the resonance structures with a pyridine ring to the wave function of the 2-HP molecule in dioxane and chloroform does not exceed 3%. In CD_3OD, the contribution of this structure increases to ~20%. In water, its contribution is variable and depends on the concentration. At low concentrations, the ring structure should be closer to the pyridine ring.

The same figures might have been presented by proceeding from the hypothesis of tautomerism. In this case, however, we are obliged to adopt the point of view that the equilibrium is markedly shifted to favor 2-hydroxypyridine in aqueous solutions. The information available in the literature [1-4] and the results of a study of the UV spectra [5, 6] and electroreduction rather definitely reject the latter point of view and make it possible to give preference for the assertion of the existence of 2-HP in a single mesomeric form. If this is so, our experimental results make it possible to draw the important conclusion that the chemical formula of 2-HP or, in other words, the relationship between the resonance structures that describe the state of the molecule depends markedly on the nature of the solvent and the concentration of the dissolved 2-HP.

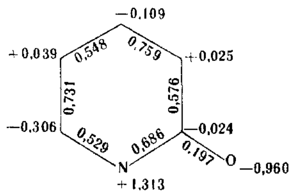
Since the UV spectrum of 2-HP in aqueous and alcohol solutions differs sharply from the spectrum of 2-methoxypyridine and is close to the spectrum of 1-methylpyridone, it can apparently be assumed that we are dealing with a mesomeric structure (V) with separated charges and appreciable aromatic character of the ring which in a certain sense, is a zwitterion.



V

Calculation with the Pople π approximation of the zwitterion model with the bond lengths and semiempirical parameters of 2-pyridone, but with an increased ionization potential of the carbonyl oxygen and a decreased ionization potential of the pyrrole nitrogen, led to the distribution of the π-electron charges depicted by diagram VI. (See scheme on the following page.) The molecular diagram (VII) of a zwitterion model with the fundamental parameters of 2-hydroxypyridine, except for the increased ionization potential of the pyridine nitrogen and the decreased ionization potential of the "ester" oxygen, was calculated simultaneously.

The results of the calculation of the distribution of the π charges in models of the 2-pyridone and 2-hydroxypyridine molecules, respectively, are presented in diagrams VIII and IX. It may be noted that the signs of the π charges of the carbon atoms in both molecules coincide. The charges in the 3 and 5 positions change places on passing from the pyridine (IX) to the pyridone (VIII) ring, and are more equalized in the



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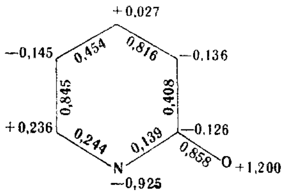

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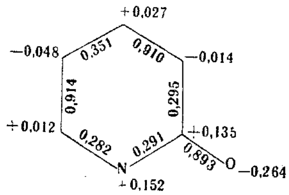

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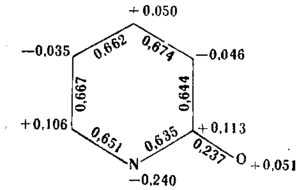

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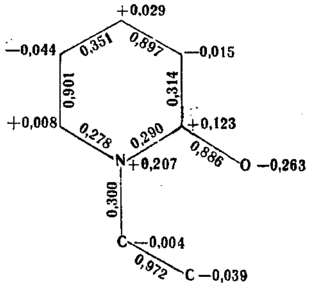

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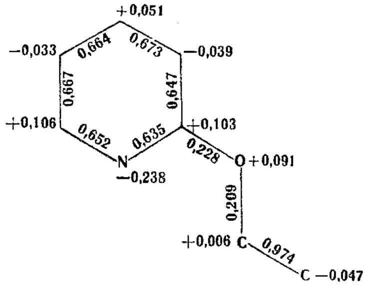


XI

pyridine ring. On the other hand, the π charges in the 4 and 6 positions are closer in magnitude to those of the pyridone ring. Interesting peculiarities can be noted on examining the zwitterion models. In the case of VI, despite the alternating values of the resonance integrals of the ring C−C bonds, we obtained a structure with more or less equalized bond orders. The charges in the 3 and 5 positions of the ring are positive. (The small shift in the signals to weak field in the PMR spectra should correspond to this.) In the case of VII, on the other hand, the use of the same C−C resonance integrals led to an appreciable alternation of the bond orders. The charges in the 3 and 5 positions are negative. On the whole, the results are additional proof in favor of the idea that the state of the 2-HP molecule in aqueous and alcohol solutions is reflected to a certain degree by resonance structure IV (diagram VII). The 2-pyridone molecule, which according to the calculation, has a considerable plus charge on nitrogen, a minus charge on the oxygen, and $N-C_2$, $N-C_6$, C_2-C_3, and C_4-C_5 bond orders averaging ~0.3, has several zwitterion characteristics.

We also studied the vinyl derivatives of 2-hydroxypyridine and 2-pyridone. In molecular diagrams X and XI it is seen that the vinyl group in the ether is somewhat more polar. The distribution of the π charges in the ring changes only slightly with respect to the starting molecules.

The calculation of the electronic spectra of the investigated compounds and comparison of them with the data on UV absorption (Table 2 and Figs. 2 and 3) seems of interest.

All of the compounds have two absorption bands. In addition, a small inflection on the descending portion of the short-wave band (~255 nm) can be isolated in the UV spectrum of 1-vinyl-2-pyridone (in alcohol). In cyclohexane, the short-wave band of this compound displays a finer structure (at 225 and 235 nm). The spectrum of 2-ethoxypyridine almost coincides with the absorption of 2-vinyloxypyridine with respect to the position of the bands. At the same time, as a result of a comparison of 1-vinyl-2-pyridone with data [6] for 1-methyl-2-pyridone and with the spectrum of 2-HP in benzene, it can be seen that its long-wave band has a bathochromic shift, while the short-wave band is shifted to higher frequencies.

The electronic spectrum was calculated with allowance for all of the singly excited configurations. As can be seen, the results of this calculation basically correctly reflect the data from the spectral investigation. In the calculated spectrum of 2-pyridone, one's attention is drawn to the oscillator forces of the electronic transitions. The short-wave transition proves to be less intense. At the same time, in the calculated spectrum of 1-vinylpyridone, this transition undergoes a long-wave shift, which reduces its intensity even more. As noted, the opposite is observed experimentally. We assume that this transition may be compared with the inflection observed on the absorption curve of 1-vinylpyridone at 255 nm (alcohol) or at 235 (cyclohexane). In this case, it should be assumed that the short-wave band of 2-pyridone corresponds to two or more electronic transitions.

To estimate the interaction of the rings with the vinyl group, we measured the integral intensities of the stretching vibrations of the vinyl group double bond in the Raman spectrum ($J^{\infty}_{C=C}$). In [7], it was demonstrated that the phenyl radical may interact with the vinyl group in vinyl aryl ethers, thus changing the $J^{\infty}_{C=C}$ value. However, a substantial increase in intensity was observed with respect to the vinyl phenyl ether (80 units/mole)* only in the vinyl ethers of p-phenylphenol (245 units/mole) and p-nitrophenol (200 units/mole). The measured $J^{\infty}_{C=C}$ value for 2-vinyloxypyridine was 315 units/mole, which is higher by a factor of four than for vinyl phenyl ether. This result confirms the presence of dynamic conjugation between the ring and double bond π-electron systems through the ether oxygen atom.

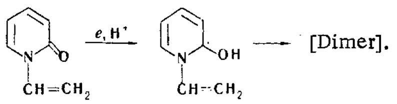
The intensity of $J^{\infty}_{C=C}$ in 1-vinyl-2-pyridone also has a high value (405 units/mole) close to the value observed in styrene, which also is evidence for strong dynamic interaction of the vinyl group and the pyridone ring.

The PMR spectra of the vinyl compounds studied are presented in Table 1. The signals of the H_A and H_B protons are found at strongest field. The H_X signal is shifted to weaker field. The multiplicity of the signals of these protons is due to their own spin–spin coupling, as a result of which each of them appears as a quartet. The $\delta_A - \delta_B$ and $\delta_X - 0.5\ (\delta_A + \delta_B)$ differences are 0.40 and 2.09 ppm for 2-vinyloxypyridine and 0.43 and 2.28 ppm for 1-vinyl-2-pyridone and are characteristic for the $-O-CH=CH_2$ and $>N-CH=CH_2$, groups, especially for vinyl ethers of substituted phenols. This provides a certain basis for assuming that the electronic interactions in the ground state of these molecules have features in common that are primarily determined by the p, π-conjugation scheme.

To obtain a comparison with 2-HP, we studied the polarographic reduction of 1-vinyl-2-pyridone. On a 0.1 M $(C_4H_9)_4NBr$ background, 1-vinyl-2-pyridone gave one wave that corresponds to the consumption of one electron by each molecule ($E_{1/2} = -1.862$ V). A study of the "morphology" of the polarogram demonstrates that the curve corresponds to the equation

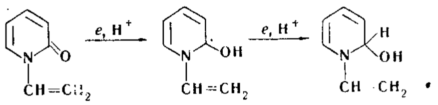
$$E=E_0-\frac{RT}{\alpha F}\ln\frac{i^{2/3}}{i_{\lim}-i}, \tag{4}$$

where E = 1.88 V, while the reciprocal slope is 85 mV, which indicates irreversibility of the reduction with subsequent rapid dimerization:



When the temperature changes by 1°, the height of the wave changes symbatically by 1.96%, which indicates the purely diffuse character of the reduction without any kinetic limitations. An increase in the dropping period leads to a decrease in the reciprocal slope of the polarogram, increasing the reversibility of the reduction, which is in agreement with the conclusions in [8].

On a 0.05 M $(C_4H_9)_4NOH$ background, 1-vinyl-2-pyridone gives two reduction waves with $E_{1/2} = -1.847$ and -2.155 V. Each of them corresponds to the absorption of one electron. The first wave corresponds to Eq. (1), in which the average slope is 67 mV, which is close to the theoretical value for reversible reduction processes (60 mV). The temperature coefficient of 2.19% per degree is evidence for the diffusion character of the reduction. Thus the scheme for the reduction of 1-vinylpyridone on a 0.05 M $(C_4H_9)_4NOH$ background can be represented in the form:



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*The J^{∞}_{313} value for 1 M CCl_4 was 100 units/mole.