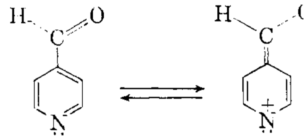
change occurs. Again, from *p*H 10.8 to 14, IIb and IIIb decrease, and IVb rapidly increases. A rather wide *p*H region between 5.9 and 10.8 is the "neutral range" of this compound.

The same treatment was employed for pyridine-3- and 4-aldehydes. The band maxima, absorbancy and ionization constants of these compounds are listed in Table I and II, respectively.

Comparison of the Three Aldehydes.—As is shown in Table I, the band maxima of Ib, IIb and IVb species in the three kinds of pyridinealdehydes are located at almost the same position, which is near to that of the π_1-band of pyridine (256 mμ). This is the expected result, since the $-CH(OH)_2$ group has little effect on the π_1-band of the pyridine ring, regardless of the position of substitution.

The neutral unhydrated form IIIb has a weak carbonyl n–π^* band in the case of 2- and 3-aldehydes but not for the 4-aldehyde. This difference may be due to the fact that the π_1-band of the 4-aldehyde is located at much longer wave length than that of the other two aldehydes, and, therefore, hides the weak n–π^* band. The longer wave length shift of the π_1-band may be due to the fact that polar resonance forms such as those shown below preferentially stabilize the excited state of the 4-aldehyde



Although similar resonance occurs in the 2-aldehyde, the inductive effect of the ring nitrogen (electron-attracting) which is opposite to the resonance effect is especially strong in the *ortho* position.

It is interesting to note that, in pyridinealdehydes, the ultraviolet spectra and ionization constants of the 2- and 3-aldehydes are similar to each other whereas that of the 4-aldehyde is different from the former two compounds. On the other hand, in hydroxypyridine, the 2- and 4-hydroxy compounds are similar and different from the 3-hydroxy compound.[5]

WORCESTER, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CLARK UNIVERSITY]

Pyridoxine and Pyridoxal Analogs. IV. Ultraviolet Spectra and Solution Equilibria of 3-Methoxypyridine-2(and 4-)-aldehydes and of 3-Hydroxypyridine-2 (and 4-)-aldehydes[1,2]

BY KAZUO NAKAMOTO AND A. E. MARTELL

RECEIVED FEBRUARY 25, 1959

The ultraviolet spectra of four new compounds, 3-methoxypyridine-2- and 4-aldehydes and 3-hydroxypyridine-2- and 4-aldehydes have been measured at various *p*H values in buffer solutions and in dioxane–water mixtures. Assignments of the absorption bands are made, and the equilibria between the various molecular species in solution are established. The over-all ionization constants are calculated from the variation of absorbancy with *p*H. From the band assignments, dissociation constants of the individual species and the equilibrium constants for their interconversion are calculated. The values obtained are compared and discussed from the viewpoint of the electronic structures of the molecules involved. The results are compared with the properties of pyridoxal and 5-desoxypyridoxal, which have been reported previously.

The ultraviolet spectra and solution equilibria of 2- and 4-hydroxymethyl-3-hydroxypyridines, and pyridine-2, 3, and 4-aldehydes have been reported in a previous publication.[3] This paper deals with more complex compounds of the same type: 3-methoxypyridine-2- and 4-aldehydes and 3-hydroxypyridine-2- and 4-aldehydes, the synthesis of which has been described recently by Heinert and Martell.[4,10] The hydroxypyridine-aldehydes are models of vitamin B_6 and are of interest in connection with the mechanism of transamination and other vitamin B_6-catalyzed reactions, studied previously by Metzler, Ikawa and Snell.[5]

Experimental

Measurements.—The experimental method is described in the preceding paper.[3]

Materials.—3-Hydroxypyridine-2- and 4-aldehydes and 3-methoxypyridine-2- and 4-aldehydes were supplied in pure form by Heinert and Martell.[4] The preparation and purification of these compounds already have been described by these authors, and therefore are not given here.

Results and Discussion

I. 3-Methoxypyridine-2- and 4-Aldehydes.—The ultraviolet spectra of 3-methoxypyridine-2-aldehyde at various *p*H values in buffer solutions are illustrated in Fig. 1. In acidic solution, two bands appear at 288 and 225.5 mμ which are assigned to the π_1- and π_2-bands of the hydrated cation, Ia, shown in Plate I. Moreover, a weak band at 316 mμ may be attributed to the π_1-band of the unhydrated cation, I'a, which is present even in 1 *N* HCl solution. The neutral solution exhibits three bands at 316, 281 and 236 mμ. Since the spectrum of this compound in pure dioxane shows two bands at 307 and 233.5 mμ, it is reasonable to attribute the bands at 316 and 236 mμ to the π_1- and π_2-bands of the uncharged unhydrated form IIIa. The remaining band at 281 mμ is therefore assigned to the π_1-band of the dipolar hydrated form IIa. The basic solution shows one strong

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[1] This investigation was supported by a research grant, H-3246, from the National Heart Institute, Public Health Service.

[2] Presented at the 134th Annual Meeting of the American Chemical Society in Chicago, Illinois, September 11, 1958.

[3] K. Nakamoto and A. E. Martell, THIS JOURNAL, **81**, 5857 (1959).

[4] D. Heinert and A. E. Martell, *Tetrahedron*, **3**, 49 (1958).

[5] D. E. Metzler, M. Ikawa and E. D. Snell, THIS JOURNAL, **76**, 648 (1954).

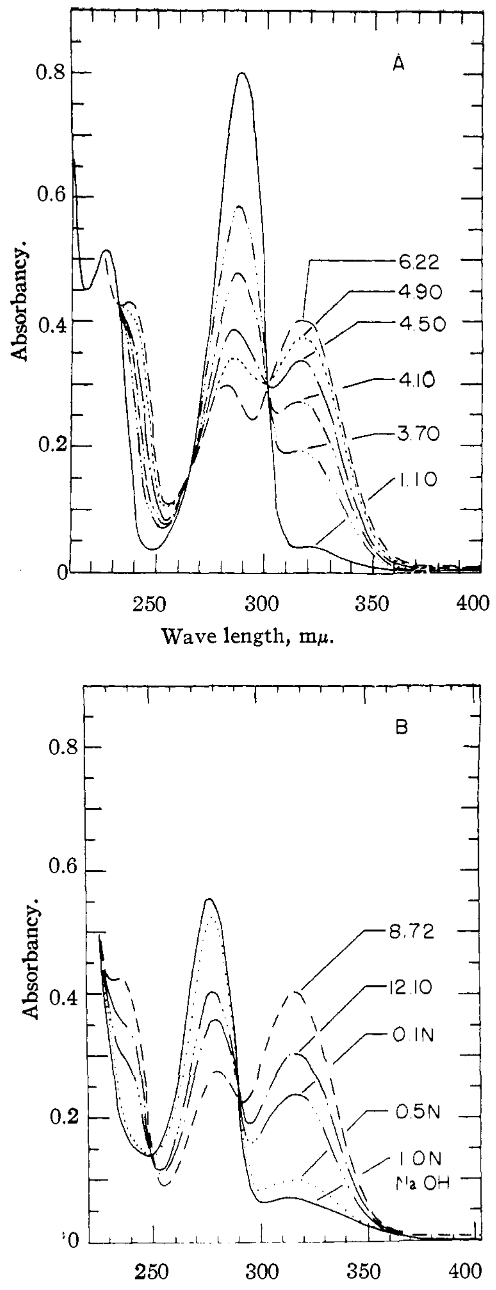

Fig. 1.—Absorption spectra of 3-methoxypyridine-2-aldehyde: A, in acidic solutions; B, in basic solutions. The numbers beside the curves denote the *p*H of the solutions.

band at 278 mμ and one weak band at 316.5 mμ. The former is attributed to the π_1-band of the hydrated anion IVa, and the latter to the π_1-band of the uncharged unhydrated species IIIa which still remains at high *p*H. Thus, the solution equilibria shown in Plate I are established.

From the comparison of the present results with those obtained for pyridine-aldehyde, it has been found that introduction of the methoxy group: 1, shifts the π_1-bands to longer wave length (see Table I), and 2, stabilizes the unhydrated form even in strongly acidic or basic solutions. The bathochromic effect of the methoxy group is known

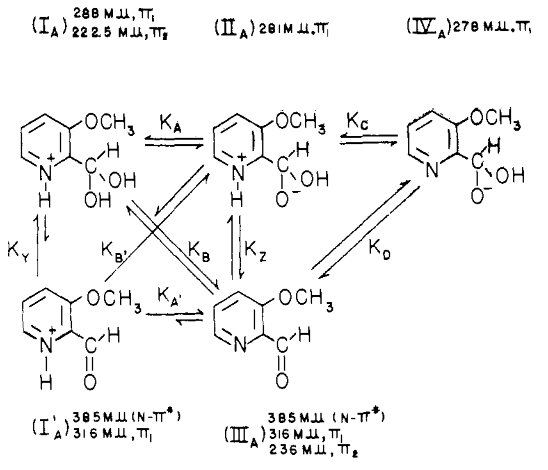

Plate I.—The solution equilibrium of 3-methoxypyridine-2-aldehyde.

for many other compounds[6] and has been discussed theoretically.[7]

The increased stability of the unhydrated form of the methoxy compound relative to the pyridine-aldehyde may be explained on the basis of its electron-donating effect. In the pyridine-aldehydes, the pyridinium nitrogen attracts electrons from the aldehyde carbon making it more positive than is the case with simple aldehydes.[8] Hydration of the aldehyde group will proceed in such a way that an oxygen of the solvent attacks the positively charged carbon. In general, the stronger the electron-attracting power of the neighboring group (atom), the aldehyde carbon becomes more positive, and the double bond character of the carbonyl bond increases.[9] It is then expected that introduction of the methoxy group cancels the electron-attracting power of the pyridinium nitrogen, since the methoxy group is electron-donating. Thus, the carbonyl group of the methoxy compound has less double bond character and is more difficult to hydrate than the corresponding pyridine-aldehyde. In accordance with this conclusion, it has been observed that the C=O stretching frequencies of pyridine-2- and 4-aldehydes in diluted carbon tetrachloride solution are 1720 cm.$^{-1}$, whereas those of the corresponding 3-methoxy compounds are 1715 and 1704 cm.$^{-1}$, respectively.[10]

Ionization Constants.—Since Ia, I′a, IIa and IIIa are involved in the complicated equilibria shown in Plate I, it is impossible to calculate the individual ionization constants rigorously. Therefore, the following assumptions have been made regarding the molecular extinction coefficients (hereafter abbreviated as ϵ). In 3-methoxypyridine-2-aldehyde, it was assumed that

$$\frac{\epsilon(\text{3-methoxypyridine[in 1 } N \text{ HCl]})}{\epsilon(\text{3-methoxypyridine-2-aldehyde[I'a]})} = \frac{\epsilon(\text{3-methoxypyridine[in dioxane]})}{\epsilon(\text{3-methoxypyridine-2-aldehyde[in dioxane]})}$$

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(6) R. A. Morton and A. L. Stubbs, *J. Chem. Soc.*, 1347 (1940).

(7) F. A. Matsen, "Chemical Application of Spectroscopy," Interscience Publishers, Inc., New York, N. Y., 1956, pp. 673.

(8) See, for example, R. N. Jones and C. Sandorfy, ref. 7, pp. 474.

(9) S. F. Mason, *J. Chem. Soc.*, 5010 (1957).

(10) D. Heinert and A. E. Martell, THIS JOURNAL, **81**, 3933 (1959).

TABLE I

COMPARISON OF THE ABSORPTION MAXIMA(mμ) OF PYRIDINE-ALDEHYDES AND THEIR METHOXY DERIVATIVES

Compound	I hydrated cation	II hydrated dipolar	III unhydrated uncharged	IV hydrated anion
Pyridine-2-aldehyde	259(π_1)	259(π_1)	320(n-π) 270(π_1) 235(π_2)	259(π_1)
	Δ = +29 mμ	Δ = +22 mμ	Δ = +46 mμ	Δ = +19 mμ
3-Methoxypyridine-2-aldehyde	288(π_1) 225.5(π_2)	281(π_1)	385(n-π) 316(π_1) 236(π_2)	278(π_1)
Pyridine-4-aldehyde	256.5(π_1)	256.5(π_1)	... 285(π_1) 224(π_2)	257(π_1)
	Δ = +28.5 mμ	Δ = +22.5 mμ	Δ = +41.5 mμ	Δ = +19 mμ
3-Methoxypyridine-4-aldehyde	285(π_1) 222.5(π_2)	279(π_1)	... 326.5(π_1) 238(π_2)	276(π_1)
Benzaldehyde	In alcohol[a]		328(n-π) 280.5(π_1) 244(π_2)	
			Δ = +29.5 mμ	
o-Methoxybenzaldehyde	In hexane[b]		310(π_1) 246.5(π_2)	

[a] A. E. Gillam and E. S. Stern, "Electronic Absorption Spectroscopy," E. Arnold (Publishers) Ltd., London, 1954, pp. 141. [b] R. A. Morton and A. L. Stubbs, *J. Chem. Soc.*, 1347 (1940).

TABLE II

ABSORPTION MAXIMA (mμ) AND ABSORBANCY OF HYDROXY AND METHOXY PYRIDINE ALDEHYDES

	Acidic		Neutral			Basic	
Pyridine derivatives	(I) cation hydrated	(I') cation unhydrated	(II) dipolar hydrated	(III) uncharged unhydrated	(III') uncharged unhydrated (in dioxane)	(IV) anion hydrated	(IV') anion unhydrated
3-Methoxy-2-aldehyde	288(0.80) 225.5(0.52)	316[a](0.04) ......[f]	281(0.30) ......[f]	385(0.01) 316(0.40) 236(0.43)	307(0.50) 233.5(0.51)	278(0.56) ......[f]	
3-Methoxy-4-aldehyde	285(0.65) 225.5(0.36)	326.5(0.02) ......[f]	279(0.28) ......[f]	326.5(0.20) 238(0.32)	322(0.43) 237(0.70)	276(0.41) ......[f]	
3-Hydroxy-2-aldehyde	287(0.79) 222(0.40)	315.5[a](0.05) ......[f]	315.5(0.45) 240(0.63)	376(0.21)[b] 260(0.25)	316(0.61) 240(0.48)		370(0.71) 250(0.67) 230(0.96)
3-Hydroxy-4-aldehyde	285(0.68) 220[a](0.42)	324(0.03) ......[f]	324(0.27) 240[a](0.58)	382(0.28)[b] 282(0.13)	330(0.36) 237(0.57)		384(0.69) 245[a](0.66)
5-Desoxypyridoxal[c]	294.5(0.65)	342(0.20)	324(0.30) 250[a](0.43)	381(0.43)[b]	......[e] ......[e]		390(0.63) 265[a](0.35)
Pyridoxal[c]	288(0.90)[d]		317(0.89)[d] 252(0.58)	390(0.01)[b]	280(0.41)	302(0.57)[d] 240(0.84)	390(0.20)

[a] Shoulder. [b] Dipolar unhydrated form. [c] Data by Metzler and Snell. [d] Hemiacetal form. [e] No spectral data. [f] Dotted lines indicate that the location of the band is not clear.

Then, $\epsilon(\text{I}'\text{a})$ was obtained as 79×10^2.[11] From this value, %(I'a) and K_y were obtained as 5 and 19, respectively, at pH 1.0. In order to determine K_z, it was assumed that $\epsilon(\text{Ia}) = \epsilon(\text{IIa})$ as in the previous paper.[3] Since, at pH 1.0, %(Ia) is 95, ϵ(Ia) at 288 mμ should be $8010 \times 100/95$, or 84×10^2. From this value, %(IIa) and K_z were obtained as 30 and 0.4, respectively, at pH 6.22, by making wing corrections for overlapping of the neighboring band at 316 mμ.

Since only 5% of I'a is present in acidic solution, its concentration was neglected without causing serious error in calculating the individual ionization constants.[12] From a plot of the pH *versus* the absorbancy, the over-all ionization constants were obtained as $pK_1 = 3.89$ and $pK_2 = 12.95$, respectively. These values were resolved into the individual ionization constants using the relations

$$K_1 = K_a + K_b;\ \frac{1}{K_2} = \frac{1}{K_c} + \frac{1}{K_d};\ K_z = \frac{K_a}{K_b} = \frac{K_d}{K_c}$$

The same procedure was employed for 3-methoxypyridine-4-aldehyde. Figure 2 indicates the spectra at various pH values in buffer solutions. Although the general feature of the spectra is similar to that of 3-methoxypyridine-2-aldehyde, the spectral difference between these two compounds is important in discussing the mechanism

(11) An alternate assumption may be as

$$\frac{\epsilon(\text{pyridine-2-aldehyde[in HCl]})}{\epsilon(\text{3-methoxypyridine-2-aldehyde[I'a]})} = \frac{\epsilon(\text{pyridine-2-aldehyde[in dioxane]})}{\epsilon(\text{3-methoxypyridine-2-aldehyde[in dioxane]})}$$

This assumption also gives a similar value for ϵ(I'a). The fact that the same values of ϵ(I'a) are obtained from two different assumptions seems to support the validity of our procedure. Considering the possible error resulting from this assumption, however, only two significant numbers were given to these values.

(12) Neglect of I'a causes only ± 0.01 pK unit difference in individual ionization constants.

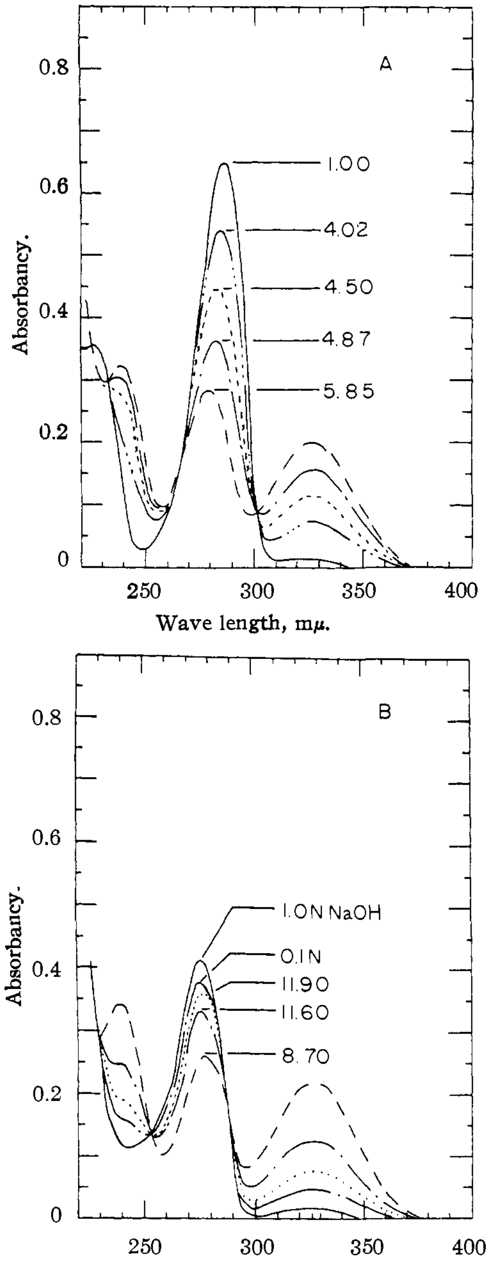

Fig. 2.—Absorption spectra of 3-methoxypyridine-4-aldehyde: A, in acidic solutions; B, in basic solutions; numbers beside the curves denote the pH of the solution.

of Schiff base formation using the spectroscopic method which will be treated in the following paper.

Dioxane–Water Mixtures.—From Fig. 3, which indicates the spectral change of 3-methoxypyridine-4-aldehyde in dioxane–water mixtures at constant pH, it is seen that the bands at 326.5 and 238 mμ (IIIa) become strong and the band at 279 mμ becomes weak as the dioxane percentage increases. This result affords additional evidence for the band assignments mentioned above, since the dipolar (IIa) and the uncharged (IIIa) forms are expected to be stable in water and dioxane, respectively. It is also noted that the bands due to the uncharged form show "red-shift" as the dielectric constant of the solvent increases (as the dioxane volume percentage decreases). These band-shifts have already been stated as a general rule in the previous paper[3] together with the possible explanation.

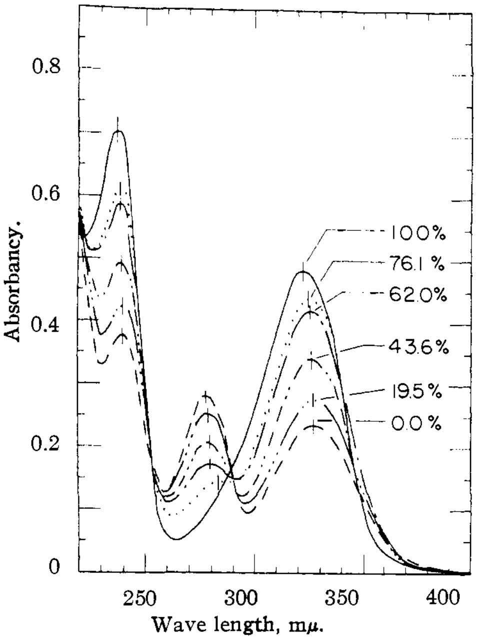

Fig. 3.—Absorption spectra of 3-methoxypyridine-4-aldehyde in dioxane–water mixtures at pH 7.0; numbers beside the curves give the volume percentage of dioxane.

II. 3-Hydroxypyridine-2- and 4-Aldehydes.—It is expected that the spectrum of 3-hydroxypyridine-4-aldehyde would be similar to those of pyridoxal and 5-desoxypyridoxal since the methyl and hydroxymethyl groups of the latter two compounds would be expected to have little effect on the spectrum. It is, therefore, interesting to compare the spectrum of 3-hydroxypyridine-4-aldehyde with those of pyridoxal and 5-desoxypyridoxal which have already been measured by Metzler and Snell.[13]

TABLE III

EQUILIBRIUM CONSTANTS

Pyridine derivatives	Over-all		Individual				
	pK_1	pK_2	pK_a	pK_b	pK^c	pK_d	K_s
2-Aldehyde	3.80	12.80	4.2	4.0	12.6	12.6	0.6[b]
3-Methoxy-2-aldehyde	3.89	12.95	4.4	4.0	12.4	12.8	0.4[b]
3-Hydroxy-2-aldehyde	3.40	6.95	3.6	3.8	6.7	6.6	1.3
4-Aldehyde	4.77	12.20	5.2	5.0	11.8	12.0	0.6
3-Methoxy-4-aldehyde	4.45	11.7	4.8	4.7	11.3	11.5	0.8
3-Hydroxy-4-aldehyde	4.05	6.77	4.4	4.2	6.4	6.6	0.6[b]
5-Desoxypyridoxal[a]	4.17	8.14	..	..	..	..	..
Pyridoxal[a]	4.20	8.66	..	..	..	..	11.5

[a] Data by Metzler and Snell (ref. 11). [b] Wing corrections for the overlapping of the neighboring band were made. For other compounds wing corrections were not necessary since the bands are far apart.

The ultraviolet spectra of 3-hydroxypyridine-4-aldehyde at various pH values are shown in Fig. 4. In acidic solution, one strong band appears at 285 mμ with another band appearing as a shoulder near 220 mμ. Since the location and the relative intensities of these bands are almost the same as those of the bands of 3-hydroxypyridine in acidic

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(13) D. E. Metzler and E. E. Snell, THIS JOURNAL, 77, 2431 (1955).

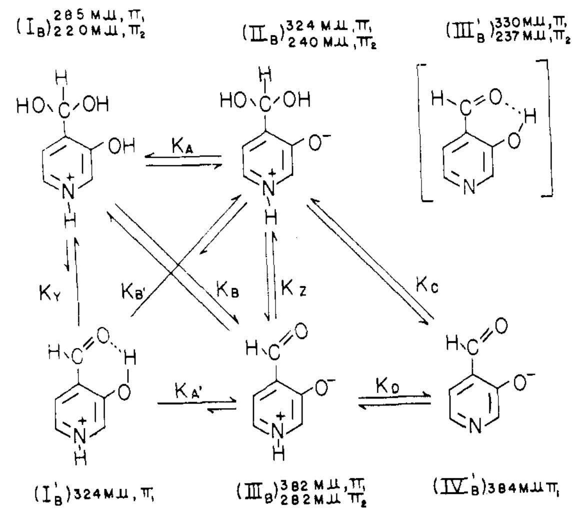

Plate II.—The solution equilibrium of 3-hydroxypyridine-4-aldehyde.

solution,[3] they are reasonably assigned to the π_1- and π_2-bands of the hydrated cation, Ib, shown in Plate II. A weak band at 324 mμ can be attributed to the π_1-band of the unhydrated cation Ib. In neutral solution, four bands appear at 382, 324, 282 and 240 mμ. Among those, the bands at 382 and 282 mμ should be ascribed to the π_1- and π_2-bands of the unhydrated form, respectively, since they are located at wave lengths which are too long to assign them to the hydrated form. However, there are two possible structures for the unhydrated form such as IIIb and IIIb'. The spectrum of this compound in pure dioxane, containing only IIIb', indicates two bands at 330 and 237 mμ. Therefore, the bands at 382 and 282 mμ are assigned to the dipolar unhydrated form, IIIb.

Then, the bands at 324 and 240 mμ can either be assigned to IIb or IIIb'. The fact[3] that the dipolar form of 3-hydroxypyridine absorbs at 313 and 248 mμ favors the former assignment. However, the latter is also possible since 3-hydroxypyridine-4-aldehyde absorbs at 330 and 237 mμ in dioxane. In such a case, a study of the band shifts in dioxane–water mixtures is useful for distinguishing between the dipolar and uncharged forms. It already has been stated as a general rule[3] that the bands due to the dipolar form show "blue-shifts," whereas the bands due to the uncharged form show "red-shifts," as the dielectric constant of the solvent increases (as the volume per cent. of dioxane decreases). Figure 5 indicates that both the bands at 382 and 324 mμ show "blue-shifts" as the dioxane percentage of the solvent decreases. Therefore, we conclude that the band at 324 mμ must be ascribed to the dipolar hydrated form IIb.[14]

Figure 5 also indicates that the 382 mμ band becomes weak and the 324 mμ band becomes strong as the dioxane percentage increases. This fact suggests that the main change caused by an increase of the dioxane percentage is a conversion of IIIb (382 mμ) into III'b (330 mμ).

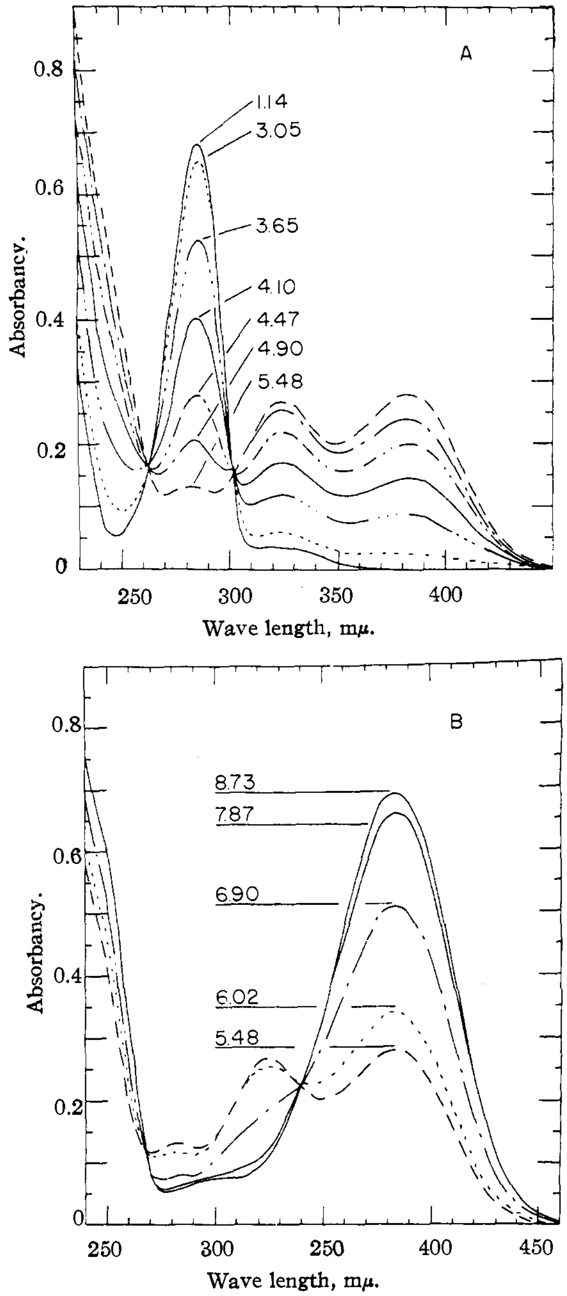

Fig. 4.—Absorption spectra of 3-hydroxypyridine-4-aldehyde: A, in acidic solutions; B, in basic solutions. The numbers beside the curves denote the *p*H of the solutions.

In basic solution, a strong band which appears at 384 mμ, and a shoulder near 245 mμ, are reasonably assigned to the unhydrated anion IVb. It is evident that almost no hydrated anion is present at high *p*H because of the fact that no appreciable absorption characteristic of the hydrated species exists near 320 mμ.

The ultraviolet spectra of 3-hydroxypyridine-2-aldehyde are shown in Fig. 6. It is seen that the spectra of the 2- and 4-aldehydes are distinctly different. As will be discussed in the subsequent paper, this difference is highly important in obtaining the imine formation constants of these two aldehydes from spectroscopic measurements.

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[14] This assignment is similar to that of Metzler and Snell[13] who attributed the bands at 381 and 324 mμ of the neutral solution of 5-desoxypyridoxal to species similar to IIIb and IIb, respectively.

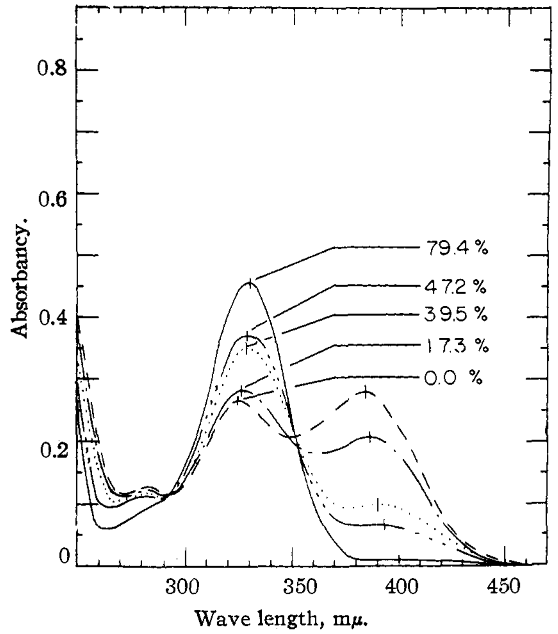

Fig. 5.—Absorption spectra of 3-hydroxypyridine-4-aldehyde in dioxane–water mixtures at pH 5.5; numbers beside the curves denote the volume percentage of dioxane.

III. Pyridoxal and 5-Desoxypyridoxal.—The ultraviolet spectra of pyridoxal and 5-desoxypyridoxal already have been measured by Metzler and Snell.[13] However, no detailed discussion was given by these authors. Based on the results we have obtained so far, the solution equilibrium shown in Plate III is proposed.

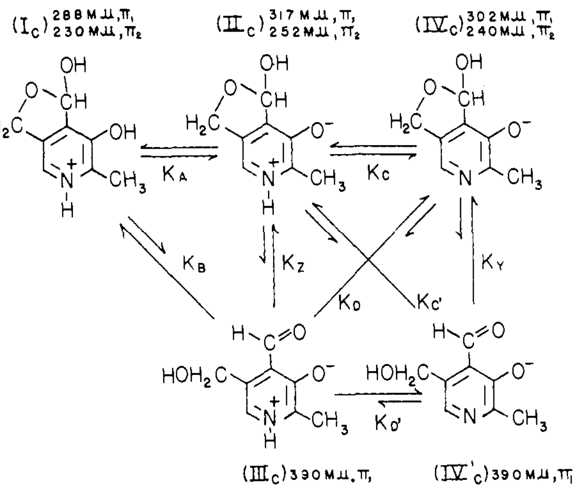

Plate III.—The solution equilibria of pyridoxal.

In acidic solution of pyridoxal, one strong band appears at 288 mμ which should be assigned to the π_1-band of the hemiacetal cation Ic.[15] Since no other bands exist, it is evident that the unhydrated form such as I′b is not present in acidic solution. In neutral solution, two bands are observed at 390 and 317 mμ, which are assigned to the dipolar unhydrated form IIIc and the dipolar hemiacetal form IIc, respectively. The fact that the 317 mμ band is exceedingly strong and the 390 mμ band is extremely weak indicates that the hemiacetal form predominates in neutral solution. In basic solution, two bands at 390 and 302 mμ are assigned to the unhydrated anion IV′c and the hemiacetal anion IVc, respectively. Again, the 302 mμ band is much stronger than the 390 mμ band indicating that the hemiacetal form predominates even in basic solution. Thus, it is

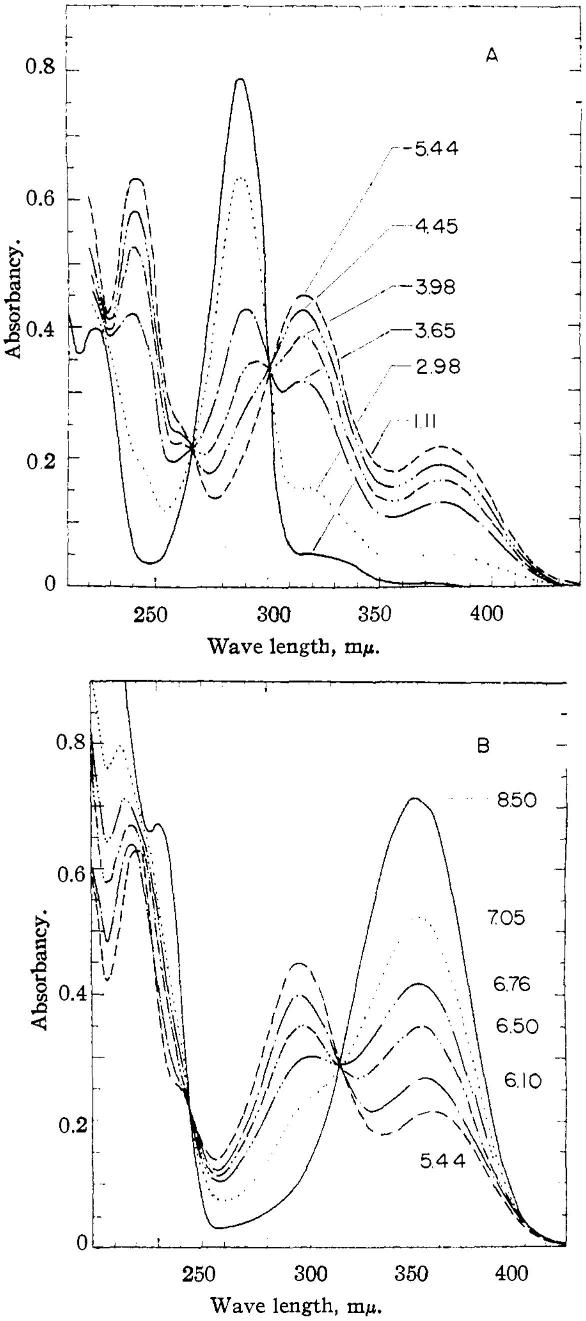

Fig. 6.—The absorption spectra of 3-hydroxypyridine-2-aldehyde; A, in acidic solutions; B, in basic solutions. The numbers beside the curves denote the pH of the solutions.

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[15] The location of this band definitely indicates that the species responsible for this band has a "hydrated" aldehyde group. It is difficult, however, to distinguish from the ultraviolet spectra between the hemiacetal and the hydrated aldehyde which has the hydroxymethyl group at the *ortho* position. We assume that the latter is unstable and forms the hemiacetal immediately.

concluded that, in the aqueous solution of pyridoxal, the hemiacetal form predominates in the whole *p*H range because of its high stability.[16]

In Table II the spectral data of 3-hydroxypyridine-4-aldehyde are compared with those of 5-desoxypyridoxal and pyridoxal. It is seen that for these three compounds, the locations of the absorption maxima of each species are quite similar, whereas the predominant species of pyridoxal at each *p*H is entirely different from those of the other two compounds. In the absence of the hydroxymethyl group in the 5-position, the amount of the unhydrated form increases as the *p*H of the solution is raised, and, at high *p*H, only the unhydrated form exists. On the other hand, in pyridoxal, only the cyclic hemiacetal form is present in acidic solutions and predominates even in basic solution.

This difference may be explained as follows: since the hydroxymethyl group is electron-attracting, the double bond character of the C=O bond of the aldehyde next to the hydroxymethyl group increases. As stated before, this favors the hydration of the aldehyde group. Then, dehydration proceeds to form the hemiacetal as

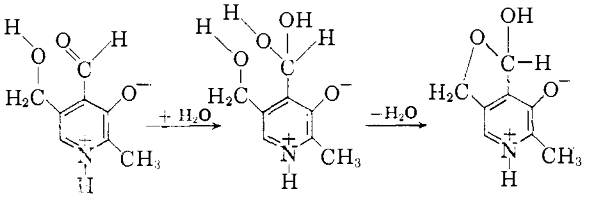

Table II compares the ionization constants of all the pyridine aldehydes studied spectroscopically. It is noted that pK_1 is always smaller in the 2-aldehyde than in the 4-aldehyde derivatives. The constant pK_1 involves the ionizations of the pyridinium hydrogen (I → III) and hydroxyl hydrogen (I → II). The former ionization is favored by the electron-attracting inductive effect of the hydrated aldehyde group, which is stronger in the *ortho* than in the *para* position. The latter ionization also proceeds more easily in the 2-aldehyde than in the 4-aldehyde since the dipolar hydrated form II of the former is stabilized by an intramolecular hydrogen bond of the type, $N^+-H\cdots O^-$.

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[16] This result is favorable for the determination of imine formation constants from spectroscopic data, since the imine band is located at 380~400 mμ where no absorption of pyridoxal exists.

[CONTRIBUTION NO. 2450 FROM GATES AND CRELLIN LABORATORIES, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Photochemical Experiments in Rigid Media at Low Temperatures. I. Nitrogen Oxides and Ozone

BY WILLIAM B. DEMORE AND NORMAN DAVIDSON

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An apparatus for studying the photolysis of substrate molecules in suspension in a frozen inert matrix at 20°K. (or 4°K.) is described. The progress of the reaction can be followed by visible-ultraviolet and by infrared spectrophotometry. Photolysis of O_3 in a nitrogen matrix at 20°K. with ultraviolet light gives N_2O. The mechanism is: $O_3 + h\nu \rightarrow O_2 + O^*$, $O^* + N_2 \rightarrow N_2O$, where O^* is an excited oxygen atom, probably $O(^1D)$. (However, the possibility that the reaction is due to O^3P atoms with excess translational energy is not fully excluded.) Photolysis of O_3 in the presence of NO_2 gives the free radical NO_3, as well as N_2O_5 and NO. Photolysis of O_3 in the presence of N_2O causes the hot atom reaction $O^* + N_2O \rightarrow 2NO$. Hot atom chemistry and transient local melting phenomena are very important for the photochemistry of rigid media at low temperatures.

There has been considerable recent interest in efforts to prepare and identify unstable species trapped in rigid solvents at low temperatures.[1-7]

Some of our experiments in the field are reported in this and in the following paper. We have not been successful in producing (and identifying) many free radicals. However, several interesting and unexpected chemical reactions have been observed upon irradiation of various photosensitive substrates trapped in a nitrogen matrix at 20°K. These observations provide insight into the general features of photochemical processes in such low temperature rigid media.

Experimental

The general technique is to deposit on a window at 20°K., by effusion, a film of nitrogen or argon plus suitable reactive chemicals. These materials can be subjected to photolysis by ultraviolet light. The chemical changes are observed by infrared and ultraviolet spectrophotometry. Alternately, one can attempt to decompose the reactive chemical in the vapor phase and trap unstable species by rapid freezing.

The Low Temperature Cell.—The apparatus consists essentially of a windowed cold finger suspended in a vacuum chamber in such a manner that gases from storage vessels may be effused onto one of the cold windows. Normally two storage vessels are used, one containing an inert material (matrix) and the other containing the "active" material. The vacuum chamber is also fitted with windows. All connections to the vacuum chamber are demountable in order that the cell may be transported, without loss of vacuum, to the spectrophotometer.

The cell, which is suitable for use with liquid helium, hydrogen or nitrogen, is shown in half section in Fig. 1. The height is twenty-six inches, and the capacity of the central coolant vessel A is about 600 ml. The liquid nitrogen jacket B also has a volume of approximately 600 ml. The coolant containers are constructed of brass, the necks are of stainless steel, and the outer vacuum jacket is of aluminum. Vacuum seals in the outer jacket are made by means of O-rings.

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