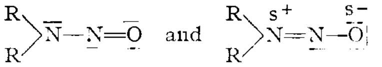
The actual structure undoubtedly is a resonance hybrid consisting of most of these forms. From the X-ray study it was concluded that structure III is of greatest significance in contributing to the final structure and in other publications[7] structure III was the only one indicated.

The absence of absorption in the 1500 cm.$^{-1}$ region indicates that the N–N bond has a considerable amount of single bond character in it. This would indicate that other structures (I or I and II) are quite significant in determining the final state of the molecule. The Raman and infrared spectra of hyponitrite ion have been reported[14] and absorption at 1392 cm.$^{-1}$ was attributed to the N–N bond. The authors interpreted this as indication of a considerable amount of single bond character in the N–N bond. Using similar arguments these studies indicate that the N–N bond in the dinitrososulfite ion has more single bond character than the N–N bond in hyponitrite for the spectra of the potassium salt in perfluorokerosene shows the absence of absorption up to 1322 cm.$^{-1}$.

The tentative assignments have been made for N–O and N–N absorption by considering the bond types to be similar to those in the dialkyl nitrosamines.[12] The following assignments have been reported for N–O and N–N vibrations in these compounds[12]: two vibrations for N–O stretch: 1315–1165 and 1265^{-1} cm.$^{-1}$; the N–N vibration between 1135–1190 cm.$^{-1}$. The structures of the nitrosamines were regarded as a hybrid of the forms



Absorptions from N=O do not occur at higher frequencies because of this resonance.

It should be kept in mind that in this study the spectra were obtained on Nujol mulls of the solid dinitrososulfites. It would be most desirable to check these measurements with Raman data on these compounds in solution to evaluate further the above assignments.

The spectra of the potassium, ammonium and sodium salts are all similar enough to indicate that the structure of the sodium salt is similar to that of the potassium and ammonium salt. With the exception of the NH_4^+ vibrations and the absorption at 1230 cm.$^{-1}$, the spectra of the potassium and ammonium salts are very much alike. The difference in the N–O vibration at 1230 cm.$^{-1}$ can be attributed to effects caused by hydrogen bonding in the ammonium salt. The existence of hydrogen bonding is further substantiated by the splitting of the N–H stretching vibration in the 3200 cm.$^{-1}$ region.

The shifts observed in the infrared spectra of the sodium salt compared to the other salts is interesting in view of the larger solubility of the sodium salt. The shifts probably arise from differences in crystal stability resulting from either anion–anion contact or from a different kind of crystal lattice in the case of the sodium salt.

URBANA, ILL.

[14] L. Kuhn and E. L. Lippincott, THIS JOURNAL, **78**, 1820 (1956).

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS OF DUKE UNIVERSITY]

Near Ultraviolet Absorption Spectra of the Pyridine Monocarboxylic Acids in Water and Ethanol Solutions[1,2]

BY HAROLD P. STEPHENSON[3] AND H. SPONER

RECEIVED DECEMBER 26, 1956

The near ultraviolet absorption spectra of picolinic, nicotinic and isonicotinic acids (2-, 3- and 4-pyridinecarboxylic acids) have been measured in 95% ethanol and distilled water solutions, and for isonicotinic acid, also for several mixtures of these two solvents. Changes in the spectra which occur when the solvent is changed from ethanol to water have been interpreted to show that the pyridine monocarboxylic acids exist primarily in the neutral, undissociated form in ethanol, and in the anion and zwitterion forms in water.[4] The spectra of the several species are discussed with regard to rather limited theoretical information concerning the effects of a carboxyl substituent on the spectrum of benzene or pyridine.

Introduction

Recently the near ultraviolet absorption spectra of the three pyridine monocarboxylic acids in aqueous solution have been reported in a number of papers,[5-7] the spectra having been observed in order to determine the acid and base dissociation constants of these substances. In each of these papers the possible zwitterion forms of the molecules were considered unimportant for an interpretation of the observed spectra. However, Jaffé[8] has discussed the tautometric equilibria of a number of substituted pyridines and their 1-oxides in aqueous solution and has concluded that nico-

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[1] Based on a portion of a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences of Duke University, 1952.

[2] This investigation was assisted by the ONR under Contract N6ori-107, T. O. I., with Duke University.

[3] Shell Oil Company Fellow in Physics, 1950–1951.

[4] For external reasons, the publication of this paper was much delayed. Before finally sending it off, a recent article by R. W. Green and H. K. Tong on "The Constitution of the Pyridine Monocarboxylic Acids in their Isoelectric Forms" (THIS JOURNAL, **78**, 4896 (1956)) has come to our attention, in which these authors came to the same conclusions about the species of these acids in aqueous solutions as are presented in this paper. However, since our approach to this problem came more from the spectroscopic side, this paper contains additional spectroscopic information which supplements the paper by Green and Tong.

[5] E. B. Hughes, H. H. G. Jellinek and B. A. Ambrose, *J. Phys. Colloid Chem.*, **53**, 414 (1949).

[6] R. F. Evans, E. F. G. Herington and W. Kynaston, *Trans. Faraday Soc.*, **49**, 1284 (1953).

[7] H. H. G. Jellinek and J. R. Urwin, *J. Phys. Chem.*, **58**, 548 (1954).

[8] H. H. Jaffé, THIS JOURNAL, **77**, 4445 (1955).

tinic acid and isonicotinic acid exist predominantly in the zwitterion form at the isoelectric point and that the thermodynamic constants K_a and K_b for these substances have been misinterpreted in the previous papers. Platt[9] has included nicotinic acid in a study of the "spectroscopic moments" of a large number of substituent groups and has suggested that observed anomalous intensities in the ultraviolet spectra of nicotinic acid may be due to zwitterion formation. In part, Platt based his conclusions on data from a spectrum which was reported to have been measured in isoöctane solution (non-polar solvent) but has since been found to have been taken in water solution instead.[10]

In this paper the near ultraviolet absorption spectra of picolinic, nicotinic and isonicotinic acids (2-, 3-, 4-pyridinecarboxylic acids) measured in this Laboratory in both ethanol and water solutions[11] will be reported which augment and clarify the arguments of Jaffé and Platt and afford an opportunity to discuss the spectra of what we think are the truly neutral species of these substances.

Experimental

The picolinic acid (melting point designated as 136°) was kindly given to us by Mr. L. Szabo of the Wyeth Institute of Applied Biochemistry. Since only a small quantity of the acid was available, it was found impossible to recrystallize any useful amount of the sample on account of the very high solubility of picolinic acid in cold water. Both the nicotinic and isonicotinic acids were purest-grade Eastman Kodak products and were used after recrystallization. In water solution where the extent of dissociation of these acids appears not to be the same for all observers, it is difficult to judge the purity of the samples by a comparison of the spectra. The absorption strength of both picolinic[12] and nicotinic[10] acid as reported by previous authors is somewhat smaller than that reported here. We have measured the spectrum of nicotinic acid both before and after recrystallization and have observed that low molar extinction values are characteristic of an unpurified sample. Better agreement between the results of different laboratories is to be expected for spectra measured in ethanol solutions, but apparently an ethanol solution spectrum has been published elsewhere only for nicotinic acid. In this case there is excellent agreement between our measured maximum molar extinction value of 2840 and an earlier value of 2820 reported by Miller.[13] All the spectra recorded in the previously mentioned papers[5-7] were measured in solutions of controlled *p*H and may not therefore be used to judge the purity of our samples.

The solutions used in this research were prepared from distilled water or 95% ethanol by ordinary procedures, and the spectral measurements were made at room temperature with a Beckman quartz spectrophotometer. Readings were taken over the wave length range from about 210 mμ up to about 320 mμ. For the concentrations used to cover most of this range (4×10^{-3} to 4×10^{-4} mole/l.) there appeared to be no significant concentration effects which could not be attributed to non-linearity of the optical density scale. The results of this paper indicate, however, that a careful study of such effects over a much wider range of concentrations in water solution would undoubtedly be very worthwhile for the pyridine carboxylic acids. For isonicotinic acid an interesting band shifting effect was discovered which seemed to warrant our taking measurements in various mixtures of ethanol and water. The proportions of 95% ethanol and water were in this case measured volumetrically.

Molar extinction coefficients ϵ were calculated from the usual equation $I = I_0 \times 10^{-\epsilon c l}$, where c refers to the total concentration of the solute in moles per liter and l is the absorbing path length, absorption cells 1 cm. long being used throughout this research. The spectra are plotted in Figs. 1, 2 and 3 with wave numbers ν (reciprocal centimeters) as the abscissae and molar extinction coefficients as the ordinates. For convenient comparison the spectra of

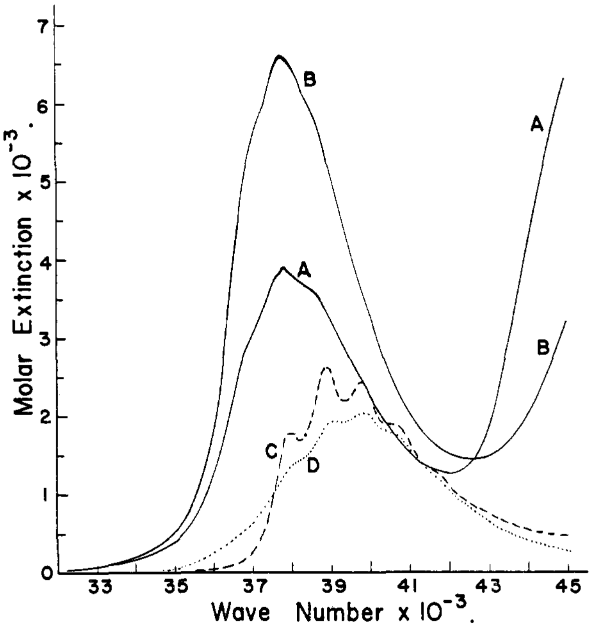

Fig. 1.—Near ultraviolet absorption spectra of: (A) picolinic acid in 95% ethanol; (B) picolinic acid in distilled water; (C) pyridine in 95% ethanol; (D) pyridine in isoöctane.

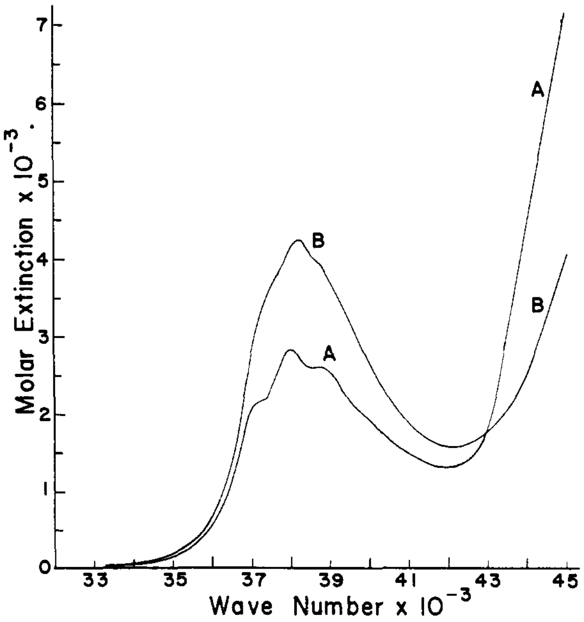

Fig. 2.—Near ultraviolet absorption spectrum of nicotinic acid in: (A) ethanol; (B) water.

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(9) J. R. Platt, *J. Chem. Phys.*, **19**, 263 (1951).

(10) API Research Project 44 at the NBS. Catalog of Ultraviolet Spectrograms. Serial No. 110, Nicotinic Acid (water solution[a]) contributed by the California Research Corporation. [a] Private communication to this Laboratory from the California Research Corporation. This spectrogram was incorrectly labelled "Solution in Isoöctane."

(11) Some of the results given here have previously been contributed to the API Catalog of Ultraviolet Spectrograms. *Cf.* Serial Nos. 231, 232, 233, 483, 484, 485.

(12) H. Hünecke, *Ber.*, **B60**, 1451 (1927).

(13) E. Miller, "Qualitative Biological Spectroscopy," Vol. I, Burgess Publishing Co., Minneapolis, Minn., 1940, p. 201.

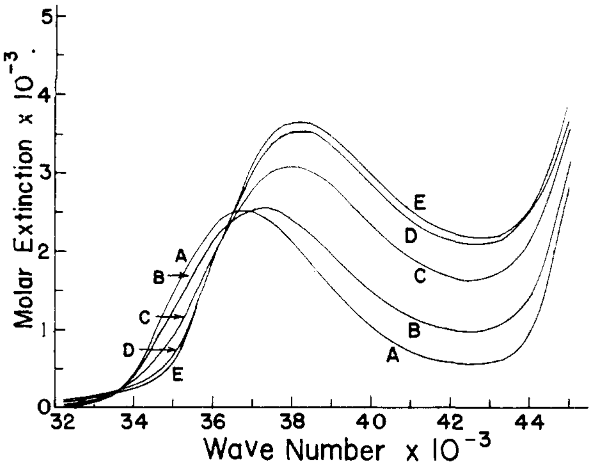


Fig. 3.—Near ultraviolet absorption spectrum of isonicotinic acid in: (A) 95% ethanol; (B) three-fourths 95% ethanol–one fourth water by volume; (C) half-and-half ethanol and water; (D) one-fourth, three-fourths mixture; (E) distilled water.

pyridine in isoöctane and ethanol solutions[14] have been included with those of picolinic acid in Fig. 1.

Recently the spectrum of pyridine in a non-polar solvent such as isoöctane (see Fig. 1D) has been interpreted as consisting of two overlapping electronic transitions, a weak n-π^* transition between 35,000 and 38,000 cm.$^{-1}$, and a strong π-π^* transition from about 37,000 to 45,000 cm.$^{-1}$, the latter transition being derived from the well-known forbidden transition of benzene.[14,15] The weak transition is due to the excitation of a non-bonding electron from the ring nitrogen,[16] and this transition shifts to higher wave numbers (shorter wave lengths) in a solution where hydrogen-bonding occurs (see Fig. 1C). Since the exact location of the shifted n-π^* transition cannot be determined, the near ultraviolet absorption spectrum of pyridine in either ethanol or water solution[17] is assumed, therefore, to be due to a single π-π^* transition of a ring π-electron.

It is likewise very probable that the single strong band appearing with a maximum at about 38,000 cm.$^{-1}$ in the spectra of the pyridine carboxylic acids is also primarily due to a single π-π^* electronic transition. The oscillator strength (f-value) of this transition is proportional to the area under the ϵ *vs.* ν graph and may be determined from the well-known equation

$$f = 4.32 \times 10^{-9} \int_0^{\infty} \epsilon d\nu$$

The f-values for the π-π^* transitions of the pyridine carboxylic acids were determined in this research by measuring areas from Figs. 1, 2 and 3 which were arbitrarily determined on the high wave number side by drawing a vertical line through the minimum of absorption around 43,000 cm.$^{-1}$. The results of the f-value determinations are listed in Table I together with the wave numbers, wave lengths and molar extinction coefficients of the band maxima.

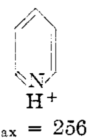
TABLE I

BAND MAXIMA AND OSCILLATOR STRENGTHS OF THE π-π^* TRANSITIONS IN THE SPECTRUM OF THE PYRIDINE MONOCARBOXYLIC ACIDS

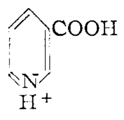
Compound	Max. wave no., cm.$^{-1}$	λ_{max}, mμ	ϵ_{max}		Solvent
Pyridine	38,900	257	2630	0.049	Ethanol
Picolinic acid	37,900	264	3900	.071	Ethanol
(2-position)	37,000	265	6600	.120	Water
Nicotinic acid	38,000	263	2840	.052	Ethanol
(3-position)	38,200	262	4230	.073	Water
Isonicotinic acid	36,800	272	2520	.055	Ethanol
(4-position)	38,200	262	3650	.093	Water

Discussion

Molecular Species in Solution.—Earlier authors[5] have called attention to the fact that the spectrum of nicotinic acid is very similar to that of pyridine and not to benzoic acid.[18] Especially impressive is the similarity of the spectra of the cations

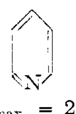


I, λ_{max} = 256 mμ
ϵ_{max} = 5320[19]
= 5290[20]

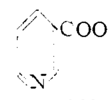


II, λ_{max} = 262 mμ
ϵ_{max} = 5500[5]
= 5000[6]

The spectra of the neutral and anion species existing in a highly basic aqueous solution (0.1 N NaOH) are likewise very similar

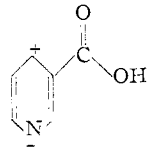


III, λ_{max} = 256 mμ
ϵ_{max} = 2660[19]
= 2750[20]



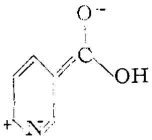
IV, λ_{max} = 262 mμ
ϵ_{max} = 2960[5]
= 3100[6]

This comparison between the spectra of pyridine and nicotinic acid indicates that the nature of the π-π^* transition in the acid is determined largely by the ring nitrogen and not by the carboxyl group. Using the symbolism of valence-bond theory, one concludes that ionic resonance structures with migration of charge to the nitrogen atom, *viz.*



V

characterize the π-π^* transition to a much larger extent than do resonance structures with migration of charge to the carboxyl group, *viz.*



VI

That structure VI plays some role in the absorption is indicated by the red shift of about 6 mμ in the maximum of the acid spectrum relative to the pyridine spectrum.[21] The corresponding red shift is particularly pronounced for isonicotinic acid and will be discussed further in the last section of this paper.

Since there is the possibility that the observed enhancement of intensity for nicotinic acid cation over that of the anion is primarily due to the addi-

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[14] H. P. Stephenson, *J. Chem. Phys.*, **22**, 1077 (1954).

[15] J. H. Rush and H. Sponer, *ibid.*, **20**, 1847 (1952).

[16] M. Kasha, *Disc. Faraday Soc.*, **9**, 14 (1950).

[17] P. Krumholz, THIS JOURNAL, **73**, 3487 (1951).

[18] H. E. Ungnade and R. W. Lamb, *ibid.*, **74**, 3789 (1952).

[19] E. B. Hughes, H. H. G. Jellinek and B. A. Ambrose, *J. Phys. Colloid Chem.*, **53**, 410 (1949).

[20] H. C. Brown and X. R. Mihn, THIS JOURNAL, **77**, 1723 (1955).

[21] (a) W. D. Kumler and L. A. Strait, *ibid.*, **65**, 2349 (1943); (b) W. F. Hammer and F. A. Matsen, *ibid.*, **70**, 2482 (1948).

TABLE II

COMPARISON OF THE ABSORPTION SPECTRA OF THE PYRIDINE MONOCARBOXYLIC ACID ANIONS AND CATIONS WITH THE SPECTRA OF OTHER DERIVATIVES NOT POSSESSING A CARBOXYL SUBSTITUENT

Compd. with carboxyl group	λ_{max}, mμ	ϵ_{max}	Compd. without carboxyl group	λ_{max}, mμ	ϵ_{max}
Picolinic acid anion	265	4000[6]	2-Picoline in 0.1 *N* NaOH	262	3560[20]
Picolinic acid cation	265	7600[6]	Same in ethanol	262	3520[14]
			Same in 0.1 *N* HCl	263	6630[20]
			2-Fluoropyridine in 0.013 *N* NaOH	257	3300[22]
			Same in ethanol	258	3200[14] 3250[23]
			Same in 1.2 *N* HCl, complete protonation not reached	260	5800[22]
Nicotinic acid anion	262	3100[6] 2960[5]	3-Picoline in 0.1 *N* NaOH	263	3110[20]
Nicotinic acid cation	262	5000[6] 5500[5]	Same in ethanol	263	3080[14]
			Same in 0.1 *N* HCl	263	5470[20]
			3-Fluoropyridine in 0.013 *N* NaOH	262	3300[22]
			Same in ethanol	262	2990[14] 3050[23]
			Same in 1.2 *N* HCl	262	5800[22]
Isonicotinic acid anion	266	2400[6]	4-Picoline in 0.1 *N* NaOH	255	2090[20]
Isonicotinic acid cation	272	4600[6]	Same in ethanol	256	2095[14]
			Same in 0.1 *N* HCl	253	4510[20]

tion of the proton to the carboxyl group rather than to the ring nitrogen, comparison data for all three of the pyridine carboxylic acids and a number of other simple pyridine derivatives not possessing a carboxyl substituent are given in Table II. The data for the fluoropyridines and picolines demonstrate that the nitrogen protonation effect is not only approximately independent of the nature of the pyridine ring substituent, but is also approximately independent of the initial degree of binding of the nitrogen non-bonding electrons. Spectral evidence[14] as well as dissociation constant measurements[22] have proved that for the *ortho*-substituted halopyridines the nitrogen non-bonding electrons are very tightly bound by an inductive effect. Whether these electrons are tightly bound or loosely bound as in the picolines,[14,20] the addition of a proton to the ring nitrogen of a pyridine derivative generally has the effect of approximately doubling the absorption intensity of the π-π^* transition in the near ultraviolet.

What the independent effect of adding or removing a proton from the carboxyl group alone would be may be estimated from the recent work of Ungnade and Lamb on benzoic acid.[18] They found that the ionization of benzoic acid in 95% ethanol solution is negligible and that ϵ_{max} is 900 at λ_{max} of 272 mμ for the π-π^* transition corresponding to the transition under discussion for the pyridine compounds. In 0.01 *N* HCl aqueous solution ϵ_{max} is 1020 at λ_{max} of 274 mμ, and in 0.01 *N* NaOH solution, where the molecule is entirely in the anion form, ϵ_{max} is 490 at λ_{max} of 268 mμ. In water solutions for which the *p*H is determined by the dissociation of the acid itself, the maximum extinction coefficient varies from 940 at a concentration of 1.748×10^{-3} mole/l. to 780 at a concentration of 0.0715×10^{-3} mole/l., for which there is considerable ionization. Thus for benzoic acid, in which the carboxyl group causes about a 5-fold intensification of the originally forbidden benzene spectrum, the relative effect of removing the proton from the carboxyl group is rather large. The relative effect will not be expected to be nearly as large for the pyridine monocarboxylic acids, however, because the *f*-value of pyridine itself is already some 50 times as large as that for benzene,[14] and the *f*-values in Table I show that the addition of the carboxyl group to pyridine serves only to increase slightly the absolute degree of absorption intensity, not its order of magnitude. One might estimate that the effect of removing a proton from the carboxyl group of the pyridine carboxylic acids would be to decrease ϵ_{max} by several hundred, possibly 200 to 500.

With a comparison of Tables I and II it becomes clear that the spectra of the pyridine carboxylic acids in ethanol solution are very similar to the spectra of the aqueous-solution anions (species IV, for example) of these substances. In spite of the fact that nearly all the carboxyl groups would, therefore, have to be dissociated, the ethanol solutions appear to be highly basic, not acidic. At first this situation seemed puzzling. It is well known that the acidity of the carboxyl group is reduced by as much as 5 *p*K_a units whenever many acids are dissolved in ethanol rather than water,[24] and therefore the spectral evidence of Ungnade and Lamb that benzoic acid is negligibly dissociated in ethanol, as well as other alcohols, is not surprising. In consequence of these facts for benzoic acid, it seems reasonable that the pyridine carboxylic acids would likewise be negligibly dissociated in ethanol solutions and that the corresponding spectra in Figs. 1, 2 and 3 actually represent the spectra of the completely neutral forms of these substances, not the anion forms. The reason the spectra are so similar to the anion spectra in all

(22) H. C. Brown and D. H. McDaniel, THIS JOURNAL, **77**, 3752 (1955).

(23) W. K. Miller, S. B. Knight and A. Roe, *ibid.*, **72**, 1629 (1950).

(24) A. J. Deyrup, *ibid.*, **56**, 60 (1934).

cases is simply that the π-electron systems of picolinic, nicotinic and isonicotinic acids are very little affected by the presence of a proton on the carboxyl group. In fact, we see that the $\epsilon_{\max}$ values for all the neutral molecules in ethanol solution are actually somewhat smaller than the $\epsilon_{\max}$ values for the corresponding anions in basic water solution, rather than larger as we would have predicted. A similar situation prevails for all the other pyridine compounds listed in Table II except 4-picoline.

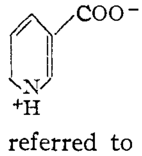
In water solution where some ionization of the pyridine acids is now expected, one sees from Figs. 1, 2 and 3 that the intensity of absorption of these acids increases with carboxyl dissociation rather than decreases as does the intensity of the benzoid acid spectrum.[18] Consequently it becomes clear why it is necessary to have established the primary importance of proton attachment at the ring nitrogen as the determining factor in the intensity changes. Every proton that detaches itself from a carboxyl group must decrease the intensity of absorption by a much smaller extent than it subsequently increases the intensity when it becomes attached to a ring nitrogen. Furthermore, there must be a large percentage of such attachments in water solution, a situation which agrees with the opinion of Jaffé[8] that these acids must exist primarily as zwitterions in water solution. According to Jaffé the neutral uncharged forms of the molecules contribute only about 5% to the equilibrium mixtures at the isoelectric points, which in each case are mixtures of rather high acidity: picolinic acid, *p*H 3.21; nicotinic acid, *p*H 3.42; isonicotinic acid, *p*H 3.31.[6] The *p*H of the water solutions used in this research will be expected to be somewhat higher than those values.

By making measurements near the isoelectric points, Evans, Herington and Kynaston[6] were able to derive spectral curves for what they called the undissociated molecular species of the acids. The curves are closely similar to the water spectra given in Figs. 1, 2 and 3, with the following values for $\epsilon_{\max}$: 7400 for picolinic acid; 4800 for nicotinic acid; 4500 for isonicotinic acid. It is significant that these $\epsilon_{\max}$ values are just 200 to 300 less than the $\epsilon_{\max}$ values of the corresponding cations listed in Table II, a difference corresponding to the change expected with the removal of a proton from the carboxyl group. Thus the evidence is rather convincing that the dissociated molecular species is formed by removing a carboxyl proton, not the ring nitrogen proton, from the cation species II. Evans, Herington and Kynaston realized that the undissociated molecular species might be an admixture of the neutral form and the zwitterion form, but they stated that it is unnecessary to discriminate between them. Such a point of view is permissible for the measurement of the apparent dissociation constants of these dibasic compounds, but the work of Jaffé shows that some discrimination is necessary for the interpretation of these constants in order to calculate the thermodynamic dissociation constants K_a and K_b.

In each of the papers[5-7] on the dissociation constants of pyridine and its derivative acids the constants which were determined experimentally were defined by the equations

$$K_1 = \frac{a \times [\mathrm{HA}]}{[\mathrm{H_2A}]} \text{ and } K_2 = \frac{a \times [\mathrm{A}]}{[\mathrm{HA}]}$$

where "a" is the hydrogen ion concentration, [HA] the concentration of the undissociated molecular species, [H_2A] the concentration of the cation species, and [A] the concentration of the anion species. If the species HA is predominantly represented by the neutral, uncharged molecule, then K_1 would be referred to as the apparent dissociation constant of the conjugate acid of the base, and K_2 would be referred to as the apparent dissociation constant of the acid. These constants were thought of in these terms by the previous authors.[5-7] On the other hand, if the species HA is predominantly represented by the zwitterion form of the molecule, for example


VII

then K_1 must be referred to as the apparent dissociation constant of the acid and K_2 as the apparent dissociation constant of the conjugate acid of the base.

From their assumptions about K_1 and K_2 the previous authors have further calculated the thermodynamic constants K_a and K_b. The most accurate results seem to be those of Evans, Herington and Kynaston, and these are summarized in Table III. According to these values of K_a and K_b, the carboxyl groups of these acids donate a proton with slightly less facility than does benzoic acid, $K_a = 6.86 \times 10^{-5}$,[18] and the basic property of the ring nitrogen is greatly reduced with respect to pyridine itself, $K_b = 1.44 \times 10^{-9}$.[25] That the basic property of the ring nitrogen appears so weak for nicotinic acid, as well as in the other two acids is the reason why Hughes, Jellinek and Ambrose[5] were the first to conclude that nicotinic acid cannot exist as a zwitterion in water solution.

TABLE III

DISSOCIATION CONSTANTS OF THE PYRIDINE MONOCARBOXYLIC ACIDS ACCORDING TO EVANS, HERINGTON AND KYNASTON[6]

Compound	pK_1	pK_2	10^5K_a	$10^{12}K_b$
Picolinic acid	1.08	5.32	0.403	0.102
Nicotinic acid	2.09	4.72	1.50	1.04
Isonicotinic acid	1.82	4.78	1.46	0.59

Jaffé has pointed out that one must know the extent of zwitterion formation before the correct values of K_a and K_b may be determined precisely from the measured K_1 and K_2 values, even when the correct interpretation of the constants is made. He finds that for nicotinic acid and isonicotinic acid the corrections are quite small because of the predominant formation of the zwitterions. With the altered interpretation of K_1 and K_2, new values of K_a and K_b may now be determined from the

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(25) E. F. G. Herington, *Disc. Faraday Soc.*, **9**, 26 (1950). See also ref. 20.

same equations used by Evans, Herington and Kynaston, namely

$$pK_a = pK_2 - \log_{10} \gamma^-$$
$$pK_b = 13.997 - pK_1 - \log_{10} \gamma^+,$$

where the values used for the activity coefficient terms were about -0.10. When the apparent dissociation constants K_1 and K_2 are interchanged in the equations, the results listed in Table IV are obtained. For example, in the case of picolinic acid

$$pK_a = 1.08 + 0.10 = 1.18$$

and consequently

$$K_a = 6.61 \times 10^{-2}$$

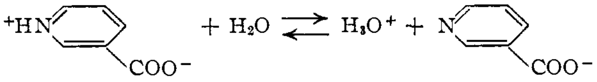
TABLE IV

DISSOCIATION CONSTANTS OF THE PYRIDINE MONOCARBOXYLIC ACIDS WITH THE ASSUMPTION THAT ZWITTERION FORMATION IS PREDOMINANT IN WATER SOLUTION

Compound	pK_a	10^2K_a	pK_b	10^9K_b
Picolinic acid	1.18	6.61	8.78	1.66
Nicotinic acid	2.19	0.646	9.38	0.417
Isonicotinic acid	1.92	1.20	9.32	0.479

These results show that the basicity of the ring nitrogen is changed very little by the introduction of the carboxyl group, but that the acidity of the carboxyl group itself is greatly enhanced by the presence of the nitrogen. These conclusions are in agreement with the spectral evidence that the ring nitrogen acts almost independently of the carboxyl substituent, preventing large migration of negative charge on to the carboxyl group as shown in resonance structure VI.

Because of the almost complete dissociation of the carboxyl groups, the pH of the water solutions used in this research must have been determined chiefly by the value of the dissociation constant K_2. That is, we are chiefly concerned with the equilibrium for which K_2 applies. Under this assumption it is possible to use the data from the paper of Evans, Herington and Kynaston to calculate theoretical values for the molar extinction coefficients of the pyridine acids in water solution. The results of these calculations are summarized in Table V. The maximum molar extinction values for the zwitterions were taken to be identical with the coefficients for the "undissociated molecular species."[6] There is good agreement between the calculated and observed values of ϵ_{max}, but for each acid the observed molar extinction coefficient is lower than the calculated value, a fact which indicates that the neutral undissociated molecular species is making a small contribution to the absorption. By assigning ϵ_{max} values to these neutral species corresponding to those obtained in ethanol solution (the values in water solution must still be considered uncertain), it appears that the neutral form makes up about 10, 5 and 15% of the *total* solute mixture in the case of picolinic, nicotinic and isonicotinic acids, respectively.



VII IV

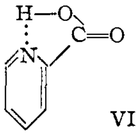
Comparison of the Spectra.—It is well known that, because of their strong electron attracting character as illustrated by the resonance structures V and VI, both a carboxyl group and a ring nitrogen are *meta*-directing substituents in benzene and pyridine. Sklar[26] has studied the effects which electron-attracting or electron-donating substituents have on the near ultraviolet π-π^* electronic transition in benzene, and was able to predict the relative intensities of the spectra of a number of isomeric disubstituted benzenes for which first-order calculations applied. While neither a ring nitrogen nor the carboxyl group fits the theoretical restrictions of the Sklar theory, Platt[9] has noted that these groups do act in a manner expected of *meta*-directing substituents in all observed cases except nicotinic acid. According to the simple Sklar treatment, one expects the oscillator strengths of the *o*- and *m*-pyridine carboxylic acids to be equal to each other and to be slightly smaller than that of pyridine itself, while the oscillator strength of *p*-pyridine monocarboxylic acid is expected to be larger than any of the other two or of pyridine itself. The equality of the oscillator strengths of the *ortho*- and *meta*-substituted compounds is predicted by the theory also for the case where the orienting powers of the substituents are different.

TABLE V

THEORETICAL CONCENTRATIONS OF VARIOUS SPECIES AND ϵ_{max} VALUES FOR WATER SOLUTIONS OF THE PYRIDINE ACIDS AT A TOTAL CONCENTRATION OF 2×10^{-4} MOLE/L.

Compound	Zwitterion concn., $\times 10^4$, mole/l.	Anion concn., $\times 10^4$, mole/l.	pH	Calcd. ϵ_{max}	Measd. ϵ_{max}
Picolinic acid	1.71	0.29	4.54	6910	6600
Nicotinic acid	1.48	.52	4.28	4360	4230
Isonicotinic acid	1.50	.50	4.30	3980	3650

Now it is significant that the oscillator strength of the electronic transition in picolinic acid should be so much larger than that of nicotinic and isonicotinic acids, regardless of whether the molecules are in their neutral forms or in the zwitterion forms characteristic of water solutions (*cf.* Table I). It is tempting to say that picolinic acid occurs predominantly in the chelated[27] form



VIII

in alcohol solution, but then it is not understandable why the oscillator strength of picolinic acid cation should continue to be so much more intense than that of nicotinic or isonicotinic acid cations. The addition of a proton to the ring nitrogen of the latter substances ought to have the effect of evening up the discrepancies between the intensities.

That the oscillator strength of isonicotinic acid should be slightly larger than that of nicotinic acid in ethanol agrees qualitatively with the results expected from the Sklar theory for two *meta*-directing substituents. This agreement must be considered very inconclusive, however, in view of the difficul-

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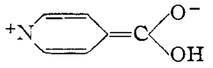
(26) A. L. Sklar, *J. Chem. Phys.*, **10**, 135 (1942), and *Rev., Modern Phys.*, **14**, 232 (1942).

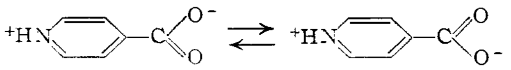
(27) N. H. Cantwell and E. V. Brown, THIS JOURNAL, **74**, 5967 (1952).

ties with the picolinic acid intensity. The observed violet shift of about 1700 cm.$^{-1}$ (*cf.* Fig. 3) which occurs for isonicotinic acid when the solution is changed from ethanol to water bears a close resemblance to the type of blue shift expected for an n-π^* transition,[14,28] but it is highly probable that the correct explanation for this blue shift is one that involves a discussion of π-electrons only. Kumler and Strait[21a] have pointed out in a discussion of the spectra of benzoic acid and *p*-aminobenzoic acid that resonance (migration of negative charge) between the carboxyl group and the ring is restricted whenever internal carboxyl resonance itself is enhanced by removal of the proton. Whereas, therefore, one expects some contribution from ionic resonance structures such as



IX (similar to VI)

in ethanol solutions, such structures will be restricted in water solution because of the added importance of the resonance



X

That is, one expects a greater migration of charge out of the ring in the neutral isonicotinic acid species than for the corresponding zwitterion species. The greater migration in the former case is a well-known explanation for the resulting shift of the π-absorption band to longer wave lengths.[21b] Since the shifts for picolinic and nicotinic acids are not so large, it can be assumed that the ionic structure IX is more important in determining the absorption by isonicotinic acid than is the corresponding structure VI for nicotinic acid (and picolinic acid). In the *ortho* and *meta*-positions the nitrogen atom undoubtedly restricts the degree of electron migration to the carboxyl group. A theoretical treatment of the perturbation effect of the carboxyl group when substituted on simple aromatic rings like benzene and pyridine is evidently very desirable.

DURHAM, NORTH CAROLINA

(28) G. J. Brealey and M. Kasha, THIS JOURNAL, **77**, 4462 (1955).

[CONTRIBUTION FROM THE MINERALS THERMODYNAMICS EXPERIMENT STATION, REGION II, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Low Temperature Heat Capacities and Entropies at 298.15° K. of Cryolite, Anhydrous Aluminum Fluoride and Sodium Fluoride

BY E. G. KING

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Heat capacities of cryolite (Na_3AlF_6), sodium fluoride and aluminum fluoride were measured in the temperature range 51 to 298°K. All showed normal behavior. The 298.15°K. entropies are: cryolite, 57.0 ± 0.4 cal./deg. mole; sodium fluoride, 12.26 ± 0.07 cal./deg. mole; and aluminum fluoride, 15.89 ± 0.08 cal./deg. mole.

This paper reports the results of heat capacity measurements throughout the temperature range 51–298°K., with derived entropies, for cryolite and its constituent fluorides. Thermodynamic values for these substances are of importance in the usual electrolytic process for aluminum production. No similar data have been published previously.

Materials.—The cryolite, supplied by the Aluminum Company of America Research Laboratories, New Kensington, Pa., consisted of hand-picked crystals of natural Greenland cryolite. The analysis by ALCOA showed 32.76% sodium (theoretical, 32.85%) and 13.01% aluminum (theoretical, 12.85%). As impurities there were 0.036% potassium and 0.007% lithium. For the purpose of the present work, the substance was considered as $Na_{2.959}AlF_{5.959}$, and the heat-capacity results were corrected to stoichiometric composition. This correlation ranged from 0.1 to 0.2%.

The sodium fluoride was Mallinckrodt analytical reagent powder meeting A.C.S. specifications. No treatment of the sample was made other than heating to 700° immediately before use.

The aluminum fluoride was a vacuum-sublimed product, prepared especially for this work by the Reduction Research Laboratory, Kaiser Aluminum and Chemical Corp., Permanente, Calif. The sample analyzed 32.12% aluminum (theoretical, 32.13%). Impurities, measured spectrographically by the Kaiser Laboratories, were: Si, 0.008%; Fe, 0.008%; Mg, 0.005%; Na, 0.05%; Ti, 0.003%; and Ca, 0.06%. All other impurities were present in amounts less than 0.003%.

Measurements and Results.—The apparatus used for these measurements has been described.[1] Sample masses employed were: cryolite, 214.48 g.; sodium fluoride, 130.08 g.; and aluminum fluoride, 241.49 g.

The heat capacities are expressed in defined calories (1 defined calorie = 4.1840 absolute joules). The measured values are given in Table I. Molecular weights accord with the 1953 International Atomic Weights.[2]

All three compounds showed normal behavior over the entire measured temperature range. It is of interest to compare the heat capacity of cryolite with that of the stoichiometric summation of sodium and aluminum fluorides. Cryolite has 60% greater heat capacity at 50°K. However, the difference decreases rapidly with temperature, becoming 7% at 100°K., less than 0.2% at 200°K., and less than 0.2% for the entire range from 200 to 298.15°K.

Entropies at 298.15°K.—The entropy increments for the measured range, 51–298°K., were obtained by Simpson-rule integrations of C_p *vs.* log T plots.

(1) K. K. Kelley, B. F. Naylor and C. H. Shomate, Bur. Mines Tech. Paper, 686, 1946.

(2) E. Wichers, THIS JOURNAL, **76**, 2033 (1954).