The results reported here may be relevant to the mechanisms of some nonredox enzymic reactions as well. Several isomerases which catalyze aldose–ketose isomerizations are metalloenzymes[36] and the function of the metal ion may be to catalyze the formation of an enediol from the α-hydroxy aldehyde or ketone. The present work indicates that Fe(III) catalyzes such a reaction even at low pH. Using the observed rate laws one can estimate that at neutral pH the Fe(III)-catalyzed enediolization would be many orders of magnitude greater than the acid-catalyzed reaction. Therefore, perhaps one of the main functions of the enzyme is to keep the metal ion in solution at higher pH's. Of course, other metal ions, or a different ionized or complexed form of Fe(III), might not be as effective catalysts as Fe(III) at pH 2. However, the results with the model system indicate that catalysis of enediolization by metal ions can occur, and thus this is a reasonable step to suggest for the enzymic reactions.

Acknowledgments. This research was supported by a research grant (AM 13448) from the National Institute of Arthritis and Metabolic Diseases, Public Health Service.

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(36) I. A. Rose in "Comprehensive Biochemistry," Vol. 17, M. Florkin and E. H. Stotz, Ed., Elsevier, Amsterdam, The Netherlands, 1969, p 107.

Thermal and Photodecarboxylation of 2-, 3-, and 4-Pyridylacetic Acid[1]

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Abstract: The 2-, 3-, and 4-pyridylacetic acids photodecarboxylate in water with high quantum efficiency. The photodecarboxylation quantum yield is a maximum at the isoelectric point and the zwitterion form is probably the ground state species absorbing 2537-Å (quartz filter) light and leading to decarboxylation. The quantum yield for photodecarboxylation of 3-pyridylacetic acid decreases with decreasing solvent polarity under 2537-Å irradiation (quartz filter), but increases with decreasing solvent polarity with a Pyrex filter. In the latter case, the nonionized ground state of the pyridylacetic acid is believed to be the absorbing species, which then leads to a zwitterion excited state before decarboxylation. Resonance stabilization of the intermediate formed from the excited state decomposition is suggested to be of little or no importance in determining the efficiency of the reaction. The 2- and 4-pyridylacetic acids decarboxylate thermally in high yield at 90°, while the 3-derivative is stable at that temperature. A maximum rate is observed at the isoelectric point and again the zwitterion form appears to be the reactive molecule. In the thermal process resonance stabilization of the intermediate formed in the decomposition is of prime importance in determining reactivity.

The liquid phase photodecarboxylations of a few, structurally quite diverse aryl-substituted acetic acids have been studied recently. Fischer[2] and later Melchior,[3] during investigations of tryptophan photodecomposition, showed that 3-indoleacetic acid aerobically photolyzed to 3-methylindole and indole, along with side chain oxidation products. Margerum observed[4] that 2-, 3-, and 4-nitrophenylacetate ions photodecarboxylated giving the same products in air or under nitrogen: 2- and 3-nitrotoluene from the 2- and 3-nitrophenylacetates and 4,4′-dinitrobibenzyl from the 4-nitrophenylacetate. Phenylacetate was found to photodecarboxylate only very slowly. On the other hand, Crosby[5] found that the aerobic photolysis of the 2-, 3-, and 4-chlorophenylacetates gave benzyl alcohol and benzaldehyde as the major products. Crosby also studied[6] aerobic and anaerobic photolyses of 1-naphthylacetate, finding in the former case 1-methylnaphthalene, 1-naphthalenemethanol, 1-naphthaldehyde, and 1-naphthoic acid and in the latter case only 1-methylnaphthalene. It was proposed that the 1-methylnaphthalene was the first product formed under both conditions. At the same time, Watkins showed[7] similar results in the aerobic case starting from 1-naphthylacetic acid rather than the acetate salt. Wang[8] found a quantitative photodecarboxylation of thymine-1-acetic acid to yield 1-methylthymine, while the corresponding uracil underwent both decarboxylation and 5,6-hydration. If these pyrimidines can be considered analogs of arylacetic acids, they fall into the same class of reactions. In summary, a pattern emerges of photodecarboxylation to yield a primary product where the carboxyl group has been replaced by hydrogen. The only exception to this was the coupled product (4,4′-dinitrobibenzyl) observed[4] from 4-nitrophenylacetate decomposition.

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(1) Photochemistry of N-Heterocycles. VII. Previous paper: F. R. Stermitz, C. C. Wei, and C. M. O'Donnell, *J. Amer. Chem. Soc.*, **92**, 2745 (1970). This work was supported in part by Grant No. GM-15425 from the National Institute of General Medical Sciences, U. S. Public Health Service.

(2) A. Fischer, *Planta*, 43, 288 (1954).

(3) G. H. Melchior, *ibid.*, **50**, 262 (1957).

(4) J. D. Margerum, *J. Amer. Chem. Soc.*, **87**, 3772 (1965); J. D. Margerum and R. G. Brault, *ibid.*, **88**, 4733 (1966); J. D. Margerum and C. T. Petrusis, *ibid.*, **91**, 2467 (1969).

(5) D. G. Crosby and E. Leitis, *J. Agr. Food Chem.*, **17**, 1036 (1969).

(6) D. G. Crosby and C. S. Tang, *ibid.*, **17**, 1291 (1969).

(7) D. A. M. Watkins, *Phytochemistry*, **8**, 979 (1969).

(8) S. Y. Wang, J. C. Nnadi, and D. Greenfield, *Chem. Commun.*, 1162 (1968).

We considered that a thorough study of the substituted pyridylacetic acids might give information on the detailed mechanism of photodecarboxylation as well as provide data on the reactivity of pyridine excited states. Because of some confusion in the literature regarding the thermal decarboxylation of these derivatives, this aspect has been included in the present study.

Experimental Section

The solvents used were reagent grade redistilled or distilled water. 4-Pyridylacetic acid hydrochloride was purchased from K & K Laboratories. 2-Pyridylacetic acid hydrochloride and 3-pyridylacetic acid were purchased from Aldrich Chemical Co., Inc. The hydrochlorides were converted to the free acids by treatment with fresh Ag_2CO_3, filtration of the resultant AgCl precipitate, precipitation of dissolved Ag with H_2S, and evaporation to dryness. Irradiations were conducted in an immersion reactor employing a Hanovia Type L (450 W) lamp or a Rayonet reactor with 2537-Å lamps. Quantum yield determinations were done with the same setups, but employing a "merry-go-round" apparatus and solutions in 13 mm i.d. tubes degassed by three freeze–thaw cycles at 0.005 Torr. Ferrioxalate actinometry provided a standard and the photodecarboxylation of 3-pyridylacetic acid was also used as a secondary actinometer. Details are reported in the Ph.D. thesis (Colorado State University, 1970) of H. W. Huang.

After completion of an irradiation, the solution was acidified and evaporated to dryness *in vacuo* at room temperature. An approximate nmr analysis of this residue was then made. The residue was brought into solution by the addition of 1 *M* H_2SO_4 and $CHCl_3$ and the $CHCl_3$ layer was discarded. The aqueous layer was brought to pH 8 and extracted several times with an equal volume of $CHCl_3$ and the $CHCl_3$ was carefully evaporated. Analysis of the final mixture of pyridines was by nmr (Varian A60-A) or gas chromatography. The 2-, 3-, and 4-methylpyridines produced by photolysis and thermolysis were identified by comparison with purchased samples and standard Sadtler infrared spectra. During short irradiations no products other than the methylpyridines and CO_2 were observed although slight yellowing of solutions occurred. Long-term irradiations resulted in extensive coloring of solutions and gradual disappearance of the pyridine-type nmr or uv spectra, indicating disruption of the pyridine ring. Products of these reactions were not investigated. Dark reactions corresponding to the irradiation experiments were conducted in each case and proved to be negative.

Solutions at varying pH values were made up by dissolving the pyridylacetic acid hydrochloride in water and then adjusting the pH to the desired value by adding standard hydrochloric acid or sodium hydroxide solution.

The following describes a typical trial preparative reaction. A solution of 0.52 g of 2-pyridylacetic acid in 300 ml of distilled water was irradiated under N_2 in the immersion reactor with a quartz insert (450-W, Type L lamp) for 2 hr. Work-up as above of the resultant solution yielded only 2-methylpyridine (91% conversion from the acid).

For the thermal decarboxylations, 15 ml of a 0.02 *M* aqueous solution of the pyridylacetic acid was added to each of six test tubes in an oil bath maintained at 90°. Analysis of the mixture (after work-up similar to above) was accomplished by nmr.

Isoelectric point and p*K* determinations were performed by titrating the pyridylacetic acid hydrochlorides in water with standard base. The pH values were determined with a type TT1C radiometer. Ultraviolet absorption spectra were determined with a Perkin-Elmer Model 402.

Results

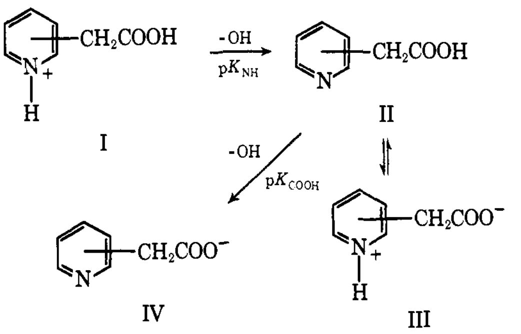
Rapid photodecarboxylation of all three pyridylacetic acids occurred in water solution (quartz, 2537 Å light). Since amino acids exist in solution as various species (eq 1) depending upon the pH of the solution, a series of exploratory (one replication) decarboxylations on each isomer at varying pH's were performed and these results are given in Table I. At the conversions listed, no significant changes in the pH of the solutions were noted. Since these runs indicated a rate maximum at or near the expected isoelectric point (p*I*), where II and III are at their highest concentrations, it was decided to determine the p*I* more exactly and then investigate the photochemistry in detail at that pH. Table II shows the results of the titrations to determine the isoelectric point.

Table I. Methylpyridine Formation from Pyridylacetic Acid (0.01 *M*) Photolyses (Quartz) at Various pH's

Isomer	pH	Irradiation time, min	Methylpyridine, %
2-Pyridylacetic acid	0.65	13	10
2-Pyridylacetic acid	2.4	10	29
2-Pyridylacetic acid	4.0	10	34
2-Pyridylacetic acid	6.0	25	20
2-Pyridylacetic acid	13.0	60	7
3-Pyridylacetic acid	0.82	30	9
3-Pyridylacetic acid	2.4	10	20
3-Pyridylacetic acid	4.2	10	27
3-Pyridylacetic acid	6.4	10	6
3-Pyridylacetic acid	13.6	60	3
4-Pyridylacetic acid	0.66	40	6
4-Pyridylacetic acid	2.6	15	15
4-Pyridylacetic acid	4.1	10	12
4-Pyridylacetic acid	6.2	25	9

Table II. Isoelectric Point Determination for Pyridylacetic Acids

Isomer	pK_{NH}	pI_{COOH}	pI
2-Pyridylacetic acid	2.46	5.58	4.02
3-Pyridylacetic acid	2.82	5.64	4.23
4-Pyridylacetic acid	2.77	5.74	4.26



(1)

The nmr of each of the acids is also pH dependent as is expected from eq 1. For example, in D_2O–DCl (where I would predominate) the complex aromatic multiplet for 3-pyridylacetic acid is found at 6.39–7.35 ppm from DDS, in NaOD–D_2O (where IV would predominate) it is at 5.79–7.0, and for the pure acid in D_2O (pH 4) the multiplet is at 6.18–7.25. Thus, the aromatic portion of the nmr at the p*I* resembles the nmr of I much more closely than it does the nmr of IV. This would be expected if III, rather than II, predominates at the p*I*. Ultraviolet absorption data confirm the presence of II and III, with III predominating, at that pH. Typical spectra are shown in Figure 1 for 3-pyridylacetic acid. It is seen from that figure that the absorption curve at pH 4 resembles the strongly acid curve (*e.g.*, from absorption by I) much more closely than it does the strongly basic curve (*e.g.*, from absorption by IV). A striking difference is noted when (as in Figure 1) the absorption curve for 3-pyridylacetic acid in methanol is compared to the absorption in methanol with strong acid or strong base added. Here the absorption curves for the basic case and the neutral molecule are similar, while that in the strongly acid solution is quite different from the neutral case. In methanol, then, II rather than III is by far the predominant species. Essentially the same results were observed by Stephenson and Sponer[9] for the pyridinecarboxylic acids where again the zwitterion form predominated in water, but the uncharged species was the major one in ethanol. Trends similar to those of Figure 1 are also observed for the 2- and 4-substituted compounds, although there are definite differences in the absorption maxima for the 2- and 3-pyridylacetic acids as compared to the 4-derivative. At pH 4, 2-pyridylacetic acid had λ_{max} 267 nm (ϵ 7600) and 3-pyridylacetic acid had λ_{max} 265 nm (ϵ 5500), while 4-pyridylacetic acid had λ_{max} 255 nm (ϵ 6700). Since the pyridine maximum under these conditions is at 257 nm, the 2- and 3-derivatives show significant bathochromic shifts while the 4-pyridylacetic acid absorption is slightly hypsochromic. This effect of substitution on pyridine absorption has been discussed[10] and is a general phenomenon not limited to the present cases.

At the isoelectric point, each pyridylacetic acid isomer gave the corresponding methylpyridine in high yield without noticeable side reactions. However, at any substantial deviation from that pH, the acids yielded additional products which were not pyridines. The typical[11] 3650-Å absorption of a 5-amino-2,4-pentadienal structure was observed to build up during these latter irradiations, but the products were not further studied. All our further studies were therefore conducted at or near pH 4, the isoelectric point.

The quantum yield for 3-methylpyridine formation (2537 Å, pH 4.0, 0.1 *M* 3-pyridylacetic acid) was determined using ferrioxalate actinometry and 3-pyridylacetic acid decomposition was then used as a secondary actinometer for similar quantum yield determinations of the other isomers. These results are shown in Table III.

Table III. Quantum Yields of Methylpyridine Formation (2537 Å, pH 4, 0.1 *M* Acid)

Compound	Quantum yield
3-Pyridylacetic acid	0.45
3-Pyridylacetic acid	0.46
2-Pyridylacetic acid	0.48
2-Pyridylacetic acid	0.49
4-Pyridylacetic acid	0.19
4-Pyridylacetic acid	0.19

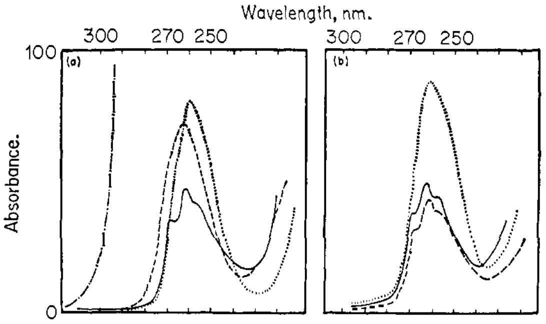


Figure 1. Absorption spectra of 3-pyridylacetic acid in water (a) and in methanol (b): ......, strongly acidic; - - - -, pH 4; ——, strongly basic; –·–·–, at 0.1 *M* concentration.

Owing to a lack of sufficient sample of the 2- and 4-pyridylacetic acids (suppliers had discontinued one or both of these derivatives), detailed studies of these isomers were indefinitely postponed. However, a number of additional experiments were conducted with 3-pyridylacetic acid. A series of quenching studies at pH 4, using air, oxygen, and biacetyl, were performed, with the results of Table IV indicating that no quenching of decarboxylation had occurred.

Table IV. Attempted Quenching of 3-Pyridylacetic Acid Decarboxylation

Acid concn, *M*	Conditions	Irradiation time, min	Per cent 3-methylpyridine formed
0.01[a]	N_2 flush	10	26
0.01[a]	Air	10	26
0.01[a]	N_2 flush	20	44
0.01[a]	Air	20	44
0.1[b]	Degassed	7.5	10
0.1[b]	Air	7.5	9
0.1[b]	Degassed	30	23
0.1[b]	Air	30	23
0.1[b]	Degassed	90	53
0.1[b]	Degassed + 0.05 *M* biacetyl	90	53
0.1[b]	Degassed + 0.1 *M* biacetyl	90	51

[a] Hanovia Type L, 450-W lamp. [b] Rayonet reactor, 2537-Å lamps.

The lack of suitable sensitizers of proper energy or absorption characteristics precluded additional work at 2537 Å. However, a tail of the absorption band of 3-pyridylacetic acid extended out of the Pyrex filter region (see Figure 1) and it was calculated that at 2950 Å in a 10% water–acetone solution 95% of the incident light would be absorbed by the acetone. Consequently a number of irradiations were performed in order to check for possible sensitization by acetone. These results are given in Table V. Thus, the photodecarboxylation

Table V. Sensitization of 3-Pyridylacetic Acid Photodecarboxylation

Conditions[a]	Irradiation time, hr	3-Methylpyridine, %
Pyrex, H_2O	1.5	20
Pyrex, H_2O	3.0	33
Pyrex, 10% acetone in H_2O	1.5	39
Pyrex, 10% acetone in H_2O	3.0	58

[a] 0.1 *M* 3-pyridylacetic acid, Hanovia Type L, 450-W lamp.

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(9) H. P. Stephenson and H. Sponer, *J. Amer. Chem. Soc.*, **79**, 2050 (1957).

(10) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962, pp 363 and 375. It is to be noted that the absorption maxima listed for pyridine, 2-picoline, and 4-picoline in water on p 363 are incorrect and should be 257, 262, and 255 nm, respectively.

(11) (a) J. Joussot-Dubien and J. Houdard-Pereyre, *Bull. Soc. Chim. Fr.*, 2619 (1969), and references therein; (b) K. E. Wilzbach and D. J. Rausch, *J. Amer. Chem. Soc.*, **92**, 2178 (1970).

proceeded with a Pyrex filter, but not as well as with quartz. Addition of acetone to absorb 95% of the light allowed the reaction to proceed nearly as well as in quartz.

Finally, because of the difference in amounts of II and III present in different solvents, a set of experiments on solvent effects at both wavelengths of light was performed (Table VI). It is apparent that the solvent effect is opposite in the two cases, with an increase in decarboxylation with solvent polarity decrease obtaining in the Pyrex filtered irradiation and the opposite effect being observed in quartz. It is to be noted that no photoalkylation products were observed when methanol was present.

Table VI. Solvent Effects on 3-Pyridylacetic Acid Photolysis (0.1 *M*)

Solvent	Filter	Irradiation time, min	3-Methylpyridine formed, %
H_2O	Quartz	30	22
H_2O	Quartz	70	44
1:1 H_2O-CH_3OH	Quartz	30	18
1:1 H_2O-CH_3OH	Quartz	70	36
H_2O	Pyrex	120	24
1:1 H_2O-CH_3OH	Pyrex	120	44

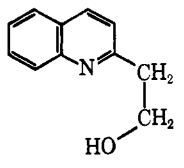
The thermal decarboxylations were studied at 90° in aqueous solution at various pH values. The 3-pyridylacetic acid did not show any decarboxylation in 10 hr at that temperature and the starting material was quantitatively recovered. However, both the 2- and 4-pyridylacetic acids decarboxylated with ease and these results are given in Table VII. Good straight-line first-order plots were obtained to greater than 80% reaction and the methylpyridines and CO_2 were the only products observed.

Table VII. Thermal Decarboxylation of Pyridylacetic Acids at 90° in H_2O

Compound	pH	Rate of methylpyridine formation, $sec^{-1} \times 10^4$
2-Pyridylacetic acid	2.3	0.63
2-Pyridylacetic acid	4.0	1.1
2-Pyridylacetic acid	6.1	0.20
4-Pyridylacetic acid	2.3	0.69
4-Pyridylacetic acid	4.3	1.4
4-Pyridylacetic acid	6.5	0.15

Discussion

Photodecarboxylation. In general terms, the photodecarboxylation fits the previously observed pattern[2-8] of overall replacement of the carboxyl function by hydrogen. Because of the structural diversity of the substrates it is questionable whether or not the same mechanism need apply to all cases. However, there are certain analogies among several of the reactions. Thus, Margerum reported[4] that the substituted nitrophenylacetic acids did not undergo photodecarboxylation, but that the corresponding acetates did. Our results, with a maximum rate at the isoelectric point, indicate a facile reaction from III, which again combines a strongly electron-withdrawing aromatic ring with the carboxylate anion. Margerum has suggested[4] a photodecarboxylation mechanism for the nitrophenylacetates based upon formation of carbon dioxide and a carbanion residue and this seems likely now to be a general mechanism since it most easily explains our data as well. In addition, we have shown[1,12] that V photoeliminates formaldehyde through the excited state VI in high quantum yield. The fact that our photodecarboxylation quantum yields fall off at high pH indicates the incursion of IV as the major species since the pyridine substituent would not be expected to be as effective in stabilizing a carbanion as the pyridinium substituent. In view of our work with V, it seems possible that the proposed zwitterionic excited state (from absorption of light by III) could also be reached directly by absorption of light from II with proton transfer in the excited state. Indeed, our results of Tables V and VI on wavelength and solvent effects seem most easily explicable on this basis. Thus, if one suggests that the reactive species at 2537 Å is III then addition of methanol (which is known to decrease the amount of III present) would cause the observed decrease in overall photodecarboxylation rate. If II is the reactive species when a Pyrex filter is employed, then the photodecarboxylation rate would increase with added methanol since the concentration of II has been shown to increase with decreasing solvent polarity. Since each of the isomers photodecarboxylated with relatively high quantum yield and showed similar pH profiles of reactivity, it seems as if a general mechanism for all isomers can be written as in eq 2.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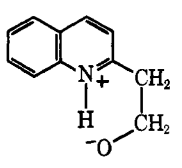
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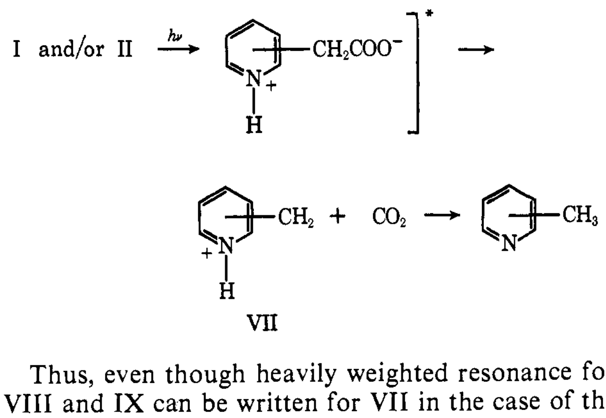

(2)

VII

Thus, even though heavily weighted resonance forms VIII and IX can be written for VII in the case of the 2- and 4-pyridyl derivatives (and cannot be written for the 3-derivative), this is unimportant for determining the quantum yield of product formation. This is also strikingly demonstrated by the nitrophenylacetate case[4] where even though intermediates X and XI are observed spectroscopically (while none is observed for

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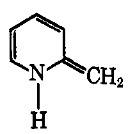
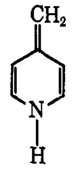
(12) C. M. O'Donnell, G. A. Knesel, T. S. Spencer, and F. R. Stermitz, *J. Phys. Chem.*, 74, 3555 (1970).

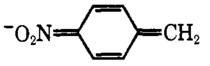


VIII

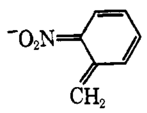


IX

the 3-nitrophenylacetate), the quantum yields of photodecarboxylation were 0.04, 0.6, and 0.6 for the 2-, 3-, and 4-nitrophenylacetates, respectively. These ideas will be contrasted with the thermal decarboxylation discussed below.



X

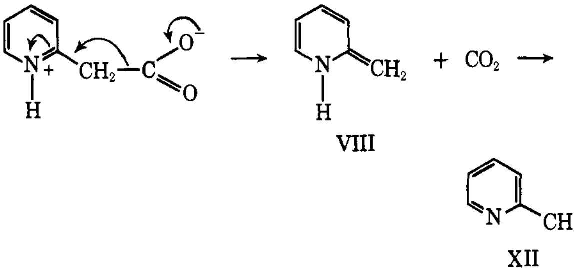


XI

Detailed investigations on the excited states involved in these reactions have been hampered by the well-known lack of emissive properties of pyridine derivatives, the lack of quenchers and sensitizers of suitable energy or water solubility, and the limited amount of 4-pyridylacetic acid available. However, the results reported for 3-pyridylacetic acid at 2537 Å showed the decarboxylation was not quenched by oxygen or biacetyl. The aerobic results are similar to those of the nitrophenylacetate cases,[4] but different from others[2,3,5–7] where the methylarenes formed from the first decarboxylation underwent further rapid oxidation. These facts, along with the postulated zwitterionic excited state, would suggest a singlet π,π^* state as the reactive one. Evidence regarding the excited states comes independently from experiments by Cundall and coworkers[13] which indicated an intersystem crossing quantum yield for pyridine of 0.3 and Lemaire,[14] who criticized the results of Cundall and suggested that the intersystem crossing quantum yields from the singlet n,π^* state and singlet π,π^* were 0.14 and 0.01, respectively. If a nonzwitterionic excited state were the reactive one in photodecarboxylation then this state would of necessity be singlet since the intersystem crossing quantum yield would be below the quantum yield for product formation. If a zwitterionic triplet state were reactive, then a markedly enhanced intersystem crossing rate for the pyridinium ion as compared to pyridine would have to be postulated. But this is opposite to what is expected since theories[15] of intersystem crossing "allowedness" invoke spin–orbit coupling in which mechanisms the nonbonded electrons of the nitrogen in the aza aromatic play an important part.

Sensitization experiments were possible only in the Pyrex-filtered irradiations and the results (Table V) showed successful sensitization by acetone. An oxygen-induced absorption band for the $T_1 \leftarrow S_0$ transition of pyridine was observed at 29650 cm^{-1} (85 kcal) by Evans,[16] while Hoover and Kasha suggested[17] that the lowest triplet of pyridine would be of slightly greater energy than that calculated from the observed[17] phosphorescence of 2,6-dimethylpyridine at 28,160 cm^{-1} (80.5 kcal). Borkman and Kearns estimated[18] the triplet energy of acetone to be 28,000 cm^{-1} (80.3 kcal), but proposed[19] acetone triplet sensitization of the isomerization of pentene-2, whose triplet should be at 29,000 cm^{-1} (83 kcal). On the other hand, acetone is also known[20] to be a singlet sensitizer. The photochemical armamentarium at the moment lacks water-soluble quenchers known to accept specifically only singlet or only triplet sensitization and which could therefore distinguish these possibilities simply. Until more detailed investigations on all isomers are at hand the question of excited states involved in the Pyrex-filtered reaction remains open.

Thermal Decarboxylation. Doering and Pasternak studied[21] the thermal decarboxylation of 2-pyridylacetic acid in water and suggested that eq 3 represented the mechanism although they could not rule out eq 4. Jurch and Ramey[22] interpreted qualitative early literature observations to mean that 4-pyridylacetic acid was harder to decarboxylate than the 2-derivative and reported[22] that 4-pyridylacetic acid did not decarboxylate in D_2O at 90° for 24 hr, although a facile decarboxylation occurred in DMSO. Equation 4, rather than eq 3, would provide a rational for the supposed reactivity difference. Our results (Table VII) show, however, that 2- and 4-pyridylacetic acid thermally decarboxylate with equal ease and with a similar pH profile. Thus, it appears that eq 3 is the best representation for the mechanism of thermal decarboxylation. Since 3-pyridylacetic acid is inert at 90°, it is to be noted that here (in contrast to the photochemical case) the availability of the heavily weighted uncharged resonance form VIII or IX is of prime importance in providing the driving force in the transition state of the thermal reaction.[23]



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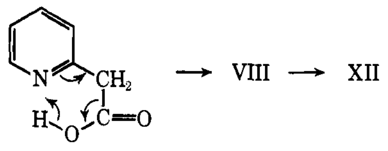

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[13] R. B. Cundall, F. J. Fletcher, and D. G. Milne, *Trans. Faraday Soc.*, **60**, 1146 (1964).

[14] J. Lemaire, *J. Phys. Chem.*, **71**, 612 (1967); *Science*, 21 (1967).

[15] M. A. El-Sayed, *J. Chem. Phys.*, **38**, 2834 (1963).

[16] D. F. Evans, *J. Chem. Soc.*, 3885 (1957).

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