A STUDY OF THE PROPERTIES OF PYRIDINECARBOXYLIC ACIDS HAVING CARBOXYL AND CARBONYL GROUPS IN POSITIONS 2 AND 3

L. P. Yurkina, N. D. Rus'yanova, L. F. Lipatova, and V. K. Kondratov

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 6, No. 3, pp. 390–393, 1970

UDC 547.826.2:543.422.46

Nonaqueous titration and a study of IR and UV spectra has enabled us to elucidate and interpret the peculiarities in the properties of pyridinecarboxylic acids which form 2, 3-substituted derivatives of pyridine. The specificity of the structure of these acids determines the peculiarity of their chemical properties: stability to the action of ozone, but exceptional ease of decarboxylation in solvents capable of disturbing the conjugated system of bonds in these acids.

In the production of nicotinic acid by the ozonolysis of quinoline and 8-hydroxyquinoline, quinolinic acid, 2-carboxypyrid-3-ylglyoxylic acid, and 3-formylpyridine-2-carboxylic acid are formed as intermediates [1]. The chemical properties of these acids, which determine the direction of the process for the preparation of nicotinic acid, have been studied to only a very small extent.

To obtain a fuller idea of the influence of the position of the carboxyl groups on the physicochemical characteristics characteristics of these compounds, we have investigated the above acids and other pyridinecarboxylic acids using nonaqueous titration and spectroscopy.

INVESTIGATION OF THE ACIDS BY TITRATION IN NONAQUEOUS MEDIA

The pyridinecarboxylic acids were titrated [2] with respect to their carboxyl groups with tetraethylammonium hydroxide in methyl ethyl ketone and in methanol and, as bases, with perchloric acid in acetic acid. The work was performed with a laboratory pH meter of the LP-58 type using glass and calomel electrodes.

It was found that in methyl ethyl ketone all the pyridinecarboxylic acids titrate satisfactorily; the monocarboxylic acids give a single jump, and the dicarboxylic acids give two, corresponding to the neutralization of the first and second carboxyl groups. For the dicarboxylic acids, the first jump is usually very small and the second considerably larger. Quinolinic and 2-carboxy-pyrid-3-ylglyoxylic acid titrate anomalously; they are characterized by a high first jump in the +100–250-mV region and a small second jump in the −300–450-mV region. These acids also exhibit peculiarities on titration with perchloric acid; in contrast to the other dicarboxylic acids and pyridinemonocarboxylic acids they do not titrate with respect to the nitrogen. 3-Formylpyridine-2-carboxylic acid also does not titrate with respect to nitrogen; and on titration with respect to the carboxyl group it gives a jump which begins in the region of the first jump of quinolinic acid and not that of the monocarboxylic acids, which begin to titrate at higher potentials.

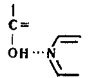
The relative strength of quinolinic acid rises markedly in methyl ethyl ketone (Fig. 1). This phenomenon is generally explained by the effect resulting from the interaction of two carboxyl groups (or a carboxyl and an aldehyde group) present in the ortho position [3].

A STUDY OF PYRIDINECARBOXYLIC ACIDS BY IR AND UV SPECTROSCOPY

The IR spectra were recorded on a UR-10 spectrometer in the 3600–500-cm^{-1} region. For recording the spectra, the substances were prepared in the form of mulls in paraffin oil and a perfluorohydrocarbon. In addition, in the 1900–1600-cm^{-1} region the IR spectra of the substances were recorded in pyridine solutions, in the 1600–1400 cm^{-1} region in methanol solutions, and in the 1800–1500-cm^{-1} region in aqueous solutions. The UV spectra were recorded on an SF-4A spectrophotometer in solution in methanol, acetic acid, and water.

A characteristic feature of the IR spectra of pyridinecarboxylic acids, in contrast to benzenecarboxylic acids, is the presence of an absorption band in the 2500-cm^{-1} region, which may be due to the appearance of dimers through the formation of a hydrogen bond between the nitrogen atom of the nucleus and the carboxyl group [4].

A hydrogen bond of this type is a hybrid of two structures.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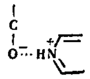
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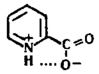
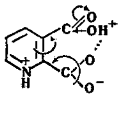
The contribution of each of the structures is obviously determined by the mutual position of the nitrogen and the carboxyl group. For nicotinic acid, structure I is probably the predominant one, and for picolinic acid, structure II, since in the IR spectrum of picolinic acid an absorption band appears at 3150 cm^{-1} which may be ascribed to the vibrations of the $\overset{+}{N}H$— bond, such a band being characteristic for the hydrochlorides of all the pyridinemonocarboxylic acids. This band is absent from the spectra of nicotinic and isonicotinic acid. The appearance of an absorption band at 3150 cm^{-1} in picolinic acid may also show the presence of an intramolecular interaction of the nitrogen of the nucleus and the α-carboxyl group.



The IR spectrum of quinolinic acid is not very similar to that of the pyridinemonocarboxylic acids (Fig. 2). A feature of the IR spectrum of quinolinic acid is the absence of a carbonyl absorption band, the presence of the broad band of a hydrogen bond in the 3070–2800 cm^{-1} region, a narrow band at 3110 cm^{-1}, and three bands at 1600, 1500, and 1380 cm^{-1} characteristic for salts of quinolinic acid and associated with the symmetrical and antisymmetrical vibrations of the COO$^-$ ion. These features are reasons for assuming that in the crystalline state quinolinic acid exists in the form of an internal salt, whose formation takes place as a result of the intramolecular interaction of the nitrogen of the nucleus and the two adjacent carboxyl groups through a π-conjugation system.



One confirmation of this structure is the IR spectrum of its potassium hydrogen salt (Fig. 3); when hydrogen is replaced by potassium the spectrum is retained completely, only the band of the hydrogen bond in the 3070–2800-cm^{-1} region disappearing. The retention in the spectrum of the absorption band of the $\overset{+}{N}H$ bond at 3110 cm^{-1} shows that no hydrogen bond exists between the α-carboxyl and the hydrogen attached to the nitrogen.

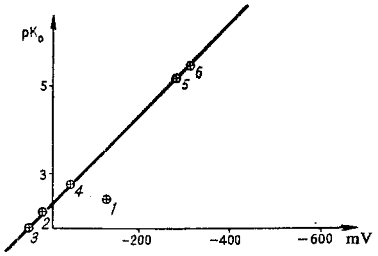


Fig. 1. Relative strengths of the pyridinecarboxylic acids in methyl ethyl ketone: 1) quinolinic acid, 2) dipicolinic acid, 3) lutidinic acid, 4) dinicotinic acid, 5) nicotinic acid, and 6) picolinic acid.

The IR spectra of the oxoacids of the pyridine series (3-formulpyridine-2-carboxylic and 2-carboxypyrid-3-ylglyoxylic acid) are similar (Fig. 3). One difference is the band of the carbonyl absorption of the aldehyde and ketone groups, which is located at 1730 cm^{-1} in 3-formylpyridine-2-carboxylic acid. This displacement of the absorption band shows its participation in the π-conjugation system and the formation of a structure similar to that of quinolinic acid. In the spectrum of the potassium salt of 3-formylpyridine-2-carboxylic acid, the carbonyl absorption is present in a region of longer wavelength, at 1700 cm^{-1}, and the hydrogen band has disappeared.

The existence of the acids in the form of internal salts in the crystalline state is a specific feature of acids which are 2, 3-substituted derivatives of pyridine. An indispensable condition for the formation of such a structure is the migration of a hydrogen ion from the α-carboxyl group to the nitrogen of the nucleus, which results in an increase in the degree of ionization of the second carboxyl group through the effect of π conjugation and the formation of a strong hydrogen bond between the two adjacent carboxyl groups. Other dicarboxylic acids do not possess this property. In pyridine-2, 4- and -3, 5-dicarboxylic acids that we studied, carbonyl absorption bands appear clearly and there are no anomalies whatever in their behavior.

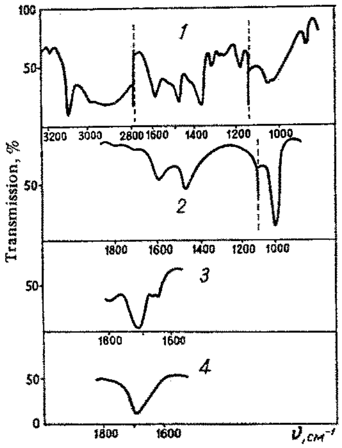


Fig. 2. IR spectra of quinolinic acid: 1) in a mull, 2) in methanol, 3) in pyridine, and 4) in water.

Quinolinic acid and the other acids having similar properties retain the internal salt structure in nonaqueous solvents. In the IR spectrum of quinolinic acid taken in a methanolic solution the carbonyl absorption band is likewise absent, and there are bands for the stretching vibrations of the COO^- ion in the 1600–1380-cm^{-1} region (Fig. 2). This structure is also confirmed by the fact that quinolinic acid cannot be titrated with respect to nitrogen in nonaqueous solvents.

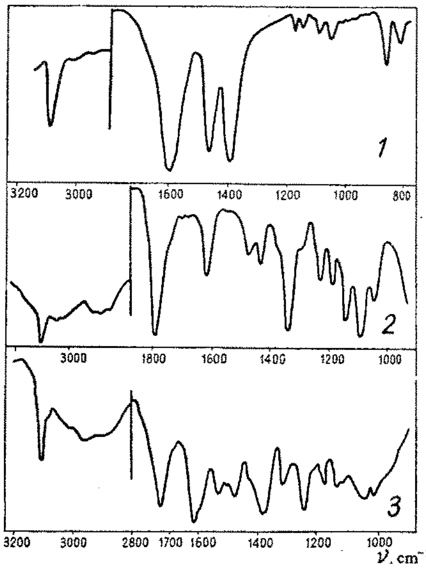


Fig. 3. IR spectra: 1) potassium hydrogen quinolinate, 2) 3-formylpyridine-2-carboxylic acid, and 3) 2-carboxypyrid-3-ylglyoxylic acid.

Pyridine and water disturb the conjugated system, and the IR spectra of quinolinic acid taken in these solvents show an absorption band for a non-ionized carboxyl group: in pyridine at 1730 cm^{-1}, and in water at 1700 cm^{-1} (Fig. 2). The shift of the carbonyl absorption band in the direction of shorter wavelengths and the absence of an absorption band for the COO^- ion which usually appears when acids dissociate in aqueous solutions [5], shows the existence of a hydrogen bond between the hydroxyl of the α-carboxyl group and the nitrogen of the nucleus, and also the possible

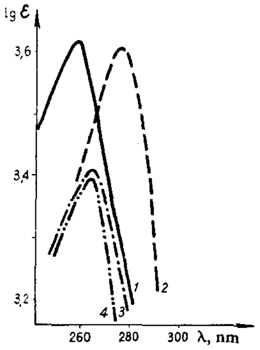
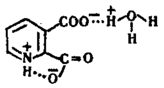


Fig. 4. UV spectra of quinolinic acid in various solvents: 1) in 90% acetic acid, 2) in water, 3) in methanol, and 4) in 100% acetic acid.

formation of a hydrate of the internal salt of quinolinic acid.



The spectra in the ultraviolet region confirm the features of the structure of the acid form in 2, 3-substituted derivatives of pyridine. In methanol all the acids have a broad absorption band in the 260–270-nm region due to $\pi-\pi^*$ transitions. For quinolinic acid, and also for the other acids having similar properties, the absorption maximum is found, as well as for picolinic acid, at 262–264 nm, but the intensity of the absorption is considerably less and is close to that of the absorption band of their potassium salts. This can apparently be explained by the greater stabilization of the π-electron system of the pyridine nucleus due to a strong hydrogen bond between the carbonyl groups and by the absence of a hydrogen bond $-\overset{+}{\mathrm{N}}\mathrm{H} \ldots \overset{-}{\mathrm{O}}-\mathrm{C}\overset{\nearrow \mathrm{O}}{\searrow}$.

In water and in aqueous acetic acid, where the formation of a hydrogen bond $-\overset{+}{\mathrm{N}}\mathrm{H} \ldots \overset{-}{\mathrm{O}}-\mathrm{C}\overset{\nearrow \mathrm{O}}{\searrow}$ and a disturbance of the stabilization of the π-electron system is assumed, the intensity of absorption increases markedly, and in water there is a pronounced bathochromic shift of the absorption maximum (Fig. 4).

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27 May 1968

Eastern Scientific-Research Carlson Chemical Institute,
Sverdlovsk