The Infrared Spectrum of Nicotinic Acid

LLOYD D. TAYLOR

Chemical Research Laboratories, Polaroid Corporation, Cambridge 39, Massachusetts

Received April 16, 1962

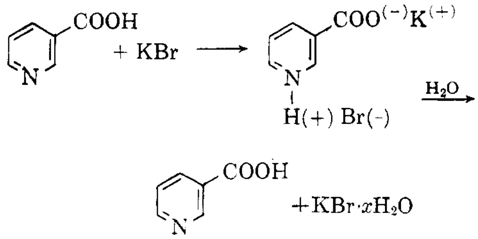
During the course of a synthetic program aimed at making vinyl nicotinate,[1] we routinely measured the infrared spectrum of nicotinic acid in potassium bromide. The spectrum showed abnormal bands at 1640 cm.$^{-1}$ (shoulder at 1620 cm.$^{-1}$) and 1380 cm.$^{-1}$, as well as a normal carbonyl band at 1710 cm.$^{-1}$. A second spectrum on the same disk after several minutes showed no abnormal bands and a more intense carbonyl absorption (see Fig. 1). The initial spectrum also showed an intense band at 3400 cm.$^{-1}$ which decreased in intensity as the disk was allowed to stand. An obvious explanation is that the new bands are due to carboxylate ion C—O asymmetrical and symmetrical stretching and possibly N—H stretching. As the disk picks up moisture from the air, the nicotinic acid reverts completely from a zwitterion to the nonionic form. Preparation of a disk without simultaneous evacuation led to a normal spectrum. Several possible variables were immediately considered and studied in an effort to explain the effect.

The hypothesis that a combination of pressure and vacuum causes zwitterion formation (which is reversed when the sample becomes wet) was first considered. Recent publications on the ultraviolet spectrum of nicotinic acid indicate that in aqueous solution nicotinic acid is a zwitterion but in ethanol is in the undissociated form.[2-4] This would seem to be opposite to our observation since moisture causes a shift to the undissociated form. We have confirmed the ultraviolet study of Stephenson and Sponer with solution infrared measurements of nicotinic acid both in deuterium oxide[5,6] and in ethanol. In the former solvent, no acid carbonyl absorption is shown but bands at 1640 cm.$^{-1}$, 1620 cm.$^{-1}$, and 1380 cm.$^{-1}$ appear. In ethanol a normal carbonyl absorption is shown at 1710 cm.$^{-1}$.

The possibility of a cation exchange between nicotinic acid and potassium bromide was considered since such exchanges with inorganic compounds have been reported.[7] Accordingly solid samples of potassium nicotinate were prepared and measured. The carboxylate ion bands occurred at much lower frequencies, ruling out the possibility of an ordinary cation exchange.

To test the importance of vacuum alone as a variable, thoroughly dried samples of nicotinic acid were measured as mulls in both Nujol and Perfluorolube. No abnormal bands were observed.

After more than forty tests, the important variables were established. The time spent in grinding the sample with potassium bromide under anhydrous conditions was found to be the determining factor, conditioned of course by the initial state of dryness of both the nicotinic acid and the potassium bromide. When preparing the disk after grinding, the importance of evacuation of the system was observed. It was also noted that the spectrum must be run immediately to avoid absorption of moisture from the air. Freshly prepared anhydrous disks placed in dessicators were shown to be stable in terms of abnormal band content but not if allowed to remain in the air. This means then that a reaction occurs which is reversed when the sample becomes wet, since samples purposely wet do not show the new bands (nicotinic acid is only very slightly soluble in water). Such a reaction scheme might be:



Disks, originally showing abnormal bands, show a normal spectrum on exposure to moisture. The abnormal bands cannot be regenerated by drying the discs at 150° over phosphorus pentoxide for forty-eight hours or by repressing. The abnormal bands can be regenerated if a regrinding operation is performed also.

The infrared spectra of various alkali metal carboxylates have been measured and are reported to show shifts in the two carboxylate ion C—O absorptions with a change in cation.[8] Accordingly, dilute deuterium oxide solution measurements of nicotinic acid were made with equivalent amounts of potassium bromide, sodium bromide, and lithium bromide present. The spectra were identical. When, however, the pellet technique was used with both sodium and lithium bromide respectively, the abnormal bands appeared but shifts of 5–10 cm.$^{-1}$ from the potassium bromide values were noted. This points to the formation of a metastable phase of nicotinic acid with the inorganic salt, whose spectrum is shifted with change in cation.

---

[1] H. C. Haas, N. W. Schuler, and L. D. Taylor, *J. Appl. Poly. Sci.*, **6**, 84 (1962).

[2] H. H. Jaffe, *J. Am. Chem. Soc.*, **77**, 4445 (1955).

[3] R. W. Green and H. K. Tong, *ibid.*, **78**, 4896 (1956).

[4] H. P. Stephenson and H. Sponer, *ibid.*, **79**, 2050 (1957).

[5] R. C. Gore, R. B. Barnes, and E. Petersen, *Anal. Chem.*, **21**, 382 (1949).

[6] E. R. Blout, *Ann. N. Y. Acad. Sci.*, **69**, 84 (1957).

[7] V. W. Meloche and G. E. Kalbus, *J. Inorg. Nucl. Chem.*, **6**, 104 (1958).

[8] L. J. Bellamy, "The Infrared Spectra of Complex Molecules,' John Wiley & Sons, New York, N. Y., 1958, p. 174.

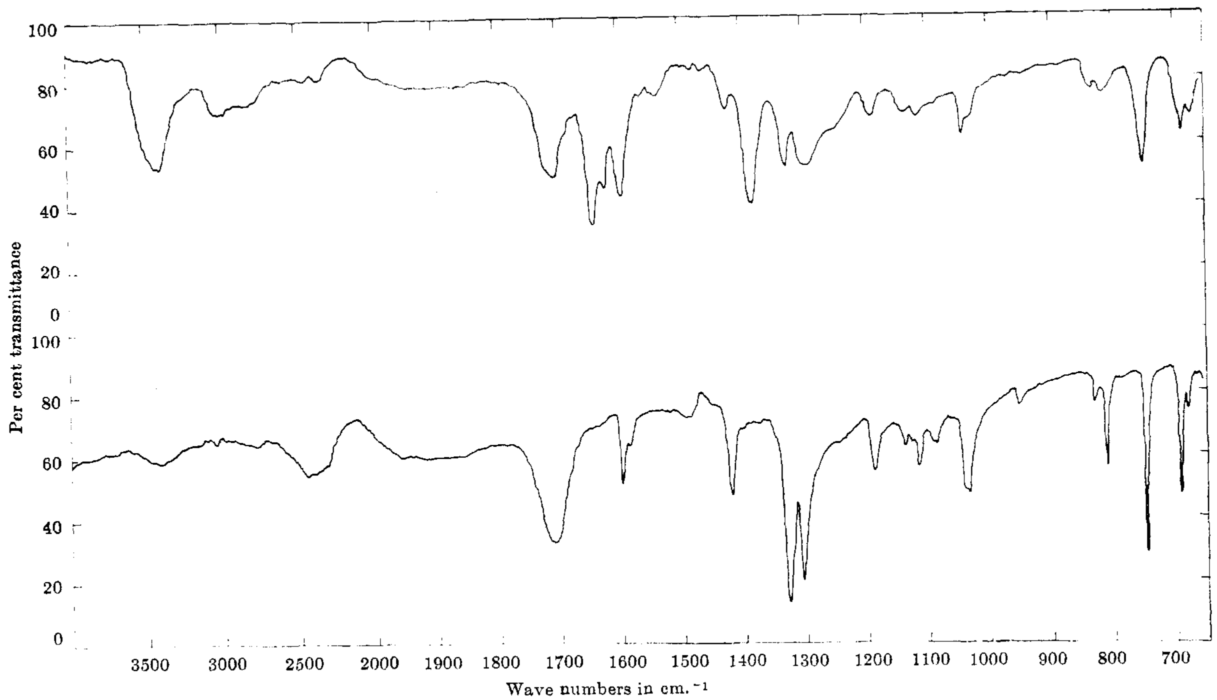


Fig. 1.—The infrared spectrum of nicotinic acid in potassium bromide: upper curve, freshly prepared disk; lower curve, same disc after standing in the air for 12 hr.

To confirm the high values for the carboxylate ion C—O stretching frequencies observed, samples of 1-methylbetaine of nicotinic acid and 1-methylbetaine of isonicotinic acid were measured.[9] These also presented high frequency values. A saturated solution of the latter compound in acetonitrile absorbs at 1630 cm.$^{-1}$.[10] The high frequencies observed are apparently the result of the positive change on the nitrogen atom.

Several experiments were performed with the isomeric picolinic and isonicotinic acids. The effect is again observable and carboxylate ion bands appear and disappear as a function of grinding time and degree of dryness of the system.

Although the potassium bromide technique is extremely valuable for measurements of solid substances, one must be cautious in interpreting a spectrum, as has been pointed out many times by other workers.[7]

Experimental

Materials.—The pyridine carboxylic acids were purest grade Eastman Kodak products and were used after several recrystallizations. The potassium bromide used was obtained from Harshaw Chemical Company. The sodium and lithium bromides were Fisher Chemicals. Both the acids and halides were heated at 100° under full vacuum for several days. They were stored in a desiccator prior to use.

Spectrophotometric Equipment.—Measurements were made with either a Perkin-Elmer infrared spectrophotometer, Model 21, or Perkin-Elmer Infracord, Model 137. The grinding apparatus used was a commercial "Wig-l-bug" manufactured by Crescent Dental Manufacturing Company. The die used for pressing disks was the Perkin-Elmer Model which is equipped for evacuation of the sample.

Measurement of Spectra.—Samples of nicotinic acid were ground with potassium bromide and pressed. Because of the sensitivity of the pellet to moisture, the spectrophotometer was preset to the region of 1750 cm.$^{-1}$, and as soon as the pellet was released from the press and vacuum, this critical region was immediately run. A typical set of conditions would be: grinding time, 1 min.; pressure, 23,000 lb., gage; evacuation, 10 min. by mechanical pump; time under pressure, 6 min.; conc., 0.3 mg. acid per 125 mg. potassium bromide. Changing these variables independently showed the following: (1) pressure, no apparent effect; (2) vacuum, very important but only a necessary condition and not the cause of the bands; (3) length of time under pressure and/or vacuum, no striking effects; (4) dryness of reagents, extemely important; and (5) grinding time, the determining variable.

The reaction of a solid with a solid would be expected to be dependent on the degree of grinding. Large differences were noted among samples ground for 0.5, 1.0, 1.5, and 2 min. It was found that the more grinding performed, the more intense the carboxylate bands. However, this trend is readily reversed if moisture gets into the grinding capsule.

Acknowledgment.—The author wishes to thank Marianne Taylor, Elizabeth Thomas, Walter Legsdin, and especially Judy Shannon, a Thayer Academy National Science Foundation summer science student, for performing the many measurements required for this study.

---

[9] E. M. Kosower and J. W. Patton, *J. Org. Chem.*, **26**, 1318 (1961).

[10] E. M. Kosower, University of Wisconsin, private communication, 1961.