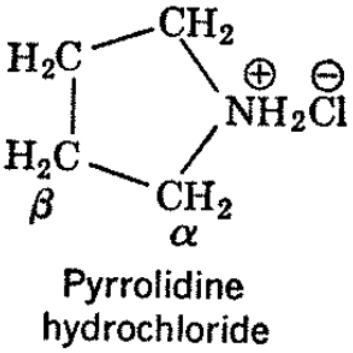
5.1: Proton Resonance Line Broadening by 14N

The broad N-H lines observed for the proton resonance spectrum (Fig. 4-16) of methylammonium ion in acid solution are worthy of special mention. Similar N-H resonances have been noted for quite a variety of substances provided the protons are not undergoing rapid exchange.[1] Pyrrolidine hydrochloride affords a particularly striking example of this behavior. The methylene protons of pyrrolidine hydrochloride in a solution containing a slight excess of pyrrolidine (Fig. 5-1) show reasonably normal spin-spin couplings. Under these circumstances, the N-H proton and the water proton resonances are averaged. Acidification of the pyrrolidine hydrochloride solution effectively stops exchange but results in broad N-H resonances which, as mentioned before in connection with methylammonium ion, could conceivably be due to intermediate proton exchange rates with the water. However, this interpretation is ruled out by virtue of the fact that Fig. 5-1 shows the N-H protons to be coupled to the a-methylene protons. If there were intermediate exchange rates, then one would expect that the N-H:C-H splittings would be washed out before the N-H resonances themselves were appreciably broadened.



Pyrrolidine hydrochloride

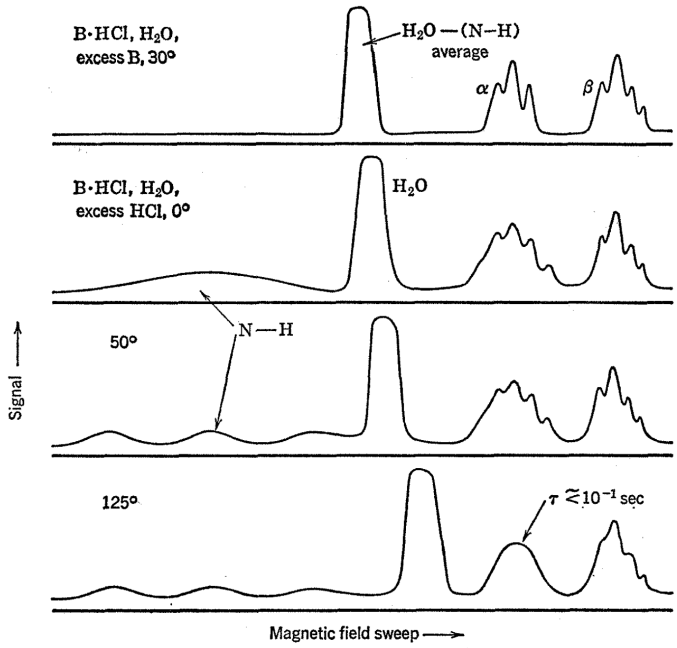


Fig. 5-1. Proton NMR spectrum of pyrrolidine hydrochloride (B·HCl) in basic and acidic solutions. Note increase in splitting of α-methylene proton resonances in acid solution. This extra splitting, which persists to above 50°, arises from magnetic interactions with the ammonium protons and shows that exchange between the ammonium and water protons is quite slow at 50° or less.

Besides being broad, the N-H resonances of substituted ammonium ions behave anomalously with temperature. Thus, lowering the temperature causes the three-line pattern to disappear and be replaced by a very broad single N-H resonance.[1] On the other hand,

raising the temperature tends to sharpen the triplet pattern, although, in any case, the lines are much broader than for the resonances of the protons of ammonium ion itself.

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1 J. D. Roberts, I. Am. Chem. Soc., 78, 4495 (1956).
