

THE HNMR SPECTRA OF MOLTEN ASYMETRIC PYRIDINIUM SALTS

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The HNMR spectrum of molten 2-methylpyridinium tetrafluoroborate was measured as a function of temperature from -15°C to 105°C on a Varian Unity 400 NMR machine. DMSO was the external standard. This salt exhibited several unusual features when compared with the 2-methylpyridinium halide melts. The N-H peak, initially at 11.08 ppm relative to TMS, broadens monotonically with increasing temperature until at around 95°C , it is so broad as to be no longer discernable. A tentative explanation for this extraordinary behavior is that some HBF_4 has left the melt and is in the vapor phase. However, when the system is cooled down, the sharp peak reappears indicating that the melt has not decomposed, even after many heating and cooling cycles. Alternatively, or in addition, the N-H proton may have become significantly delocalized so as to now be moving about the entire 2-methylpyridinium ion, but not hopping back and forth between the BF_4^- ion and the 2-methylpyridine molecule. This latter behavior is consistent with the observed integrations of the proton peaks that indicate a slight reduction in the area under the N-H peak as the temperature is increased and a concomitant increase in the area under the ring proton and methyl proton peaks.

This temperature dependence is in marked contrast to the temperature dependence of the N-H proton in 2-methylpyridinium chloride melts. In the chloride melt, the chemical shift is virtually temperature independent, but more importantly, the N-H peak *sharpens* with increasing temperature indicating that the proton is in the rapid

exchange region with respect to HNMR relaxation time and is rapidly hopping back and forth between the 2-methylpyridine ring and the chloride ion (1)

For each asymmetric salt, the anion's contributions to the HNMR spectra, and to the melt's properties generally, are discussed because it is the anion's interaction with the 2-methylpyridinium ion that largely determines these properties. To cite just one additional example, 2-methylpyridinium BF_4^- is not hygroscopic whereas 2-methylpyridinium Cl^- is very hygroscopic.

REFERENCES

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