Protonation thermochemistry of aminoacetonitrile ($NCCH_2NH_2$).[1]

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Aminoacetonitrile, a compound easily synthesized by Strecker reaction, is well-known to give the simplest aminoacid, glycine, by hydrolysis.

The gas-phase basicity, GB, of aminoacetonitrile NH_2CH_2CN has been determined from measurement of proton transfer equilibrium constants in an ion cyclotron resonance mass spectrometer (GB = 789.3$\pm$1.0 kJ.mol^{-1}). Molecular orbital calculations up to the G2 level demonstrate that protonation occurs preferentially on the nitrogen atom of the NH_2 group, and provides a theoretical proton affinity, PA, of 824.0 kJ.mol^{-1}. Exact calculation of the entropy associated with hindered rotations and consideration of Boltzman distribution of conformers allows a theoretical estimate of the molar protonation entropy $S^0(NH_2CH_2CN\text{-}H^+)$ - $S^0(NH_2CH_2CN)$ = 8.6 J.mol^{-1}.K^{-1}. Combining this value with the experimental GB leads to an "experimental" proton affinity of 819.2 kJ.mol^{-1}, in close agreement with the G2 expectation.

These results are important since the hydrolysis step of the Strecker synthesis needs, under acidic conditions, the protonation of the aminoacetonitrile. A second remark is that aminoacetonitrile is more basic than many of the other molecules expected to be present in the primitive Earth atmosphere (H_2O, CO_2, N_2, H_2 with PA values of 691, 540, 494 and 422 kJ.mol^{-1} respectively), and also than the molecules involved in the Strecker reaction (CH_2O, HCN with a common PA value of 713 kJ.mol^{-1}). An important exception however is ammonia since its proton affinity is equal to 854 kJ.mol^{-1}. In the same vein, it is noteworthy that the molecules bearing an amino group such as for example the amino acids (their PA are in the range 880-1050 kJ.mol^{-1})[2] are significantly more basic than aminoacetonitrile. All these constraints should be borne in mind when considering the possible involvement of aminoacetonitrile in gas phase processes.

[1.] G. Bouchoux, J.-C. Guillemin, N. Lemahieu, T. B. McMahon *Rapid Comm. Mass Spectrom.*, in press.[2.] E. P. Hunter, S. G. Lias J. *Phys. Chem. Ref. Data* **1998**, 413, 27.