



## “Thermochemistry of Amino Acids and Constrained Diamines”

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### Abstract

The gas-phase proton affinities of several highly basic amino acids and diamines were determined using the extended kinetic method in an ESI-quadrupole ion trap instrument. The non-protein amino acid L-canavanine is structurally related to L-arginine with an oxygen substituted for the terminal methylene group of L-arginine and is highly toxic to humans. The proton affinity of L-arginine, a protein amino acid, was determined to be  $1036 \text{ kJ mol}^{-1}$ , whereas the proton affinity of L-canavanine was determined to be  $1005 \text{ kJ mol}^{-1}$ . Thus, substitution of an oxyguanidino group for the guanidine group in L-arginine results in a large decrease in basicity. This decrease in basicity mirrors the solution behavior of these two amino acids in which the oxygen atom substitution causes a 5 pKa unit drop in basicity of L-canavanine relative to L-arginine. In addition, the proton affinities of the NPAA's L-canaline and L-citrulline were determined to be  $952 \text{ kJ mol}^{-1}$  and  $990 \text{ kJ mol}^{-1}$ , respectively. The proton affinity values presented here for the NPAA's L-canavanine, L-canaline, and L-citrulline represent the first measurements for these compounds. Experiments were complemented by high-level hybrid density functional theory calculations. Theory values obtained for proton affinities were consistent with the theoretical findings except for L-arginine, which was higher than the experimentally determined value. This may be due to the small number of reference bases in the high basicity range used to determine the experimental value.

The proton affinities of the highly basic diamines *cis*-1,5-diaminocyclooctane, tetramethylcadaverine, and hexamethylcadaverine were determined to be  $1002 \text{ kJ mol}^{-1}$ ,  $1013 \text{ kJ mol}^{-1}$ , and  $1031 \text{ kJ mol}^{-1}$ , respectively. These values are consistent with the theory that diamines display increased basicity due to the stabilization that intramolecular hydrogen bonding provides.