STUDENT 3

THE METHYLENIMMONIUM AND ETHYLIDENIMMONIUM CATIONIC HEATS OF FORMATION BY PHOTOIONIZATION MASS SPECTROMETRY

Zoë A. Harvey and John C. Traeger
Department of Chemistry
La Trobe University
Victoria 3086

It has been proposed that absolute proton affinities for the alkylimines could provide useful references for the proton affinity scale [1]. For this to occur accurate heats of formation for the corresponding cations need to be determined.

In this study, photoionization mass spectrometry is used to derive heats of formation for the two simplest protonated imine cations, methylenimmonium and ethylidenimmonium; $\Delta H_{f,298}$ ($XCHNH_2^+$); [X = H, CH_3]. The $CH_2NH_2^+$ appearance energies were determined for six amines and the $CH_3CHNH_2^+$ appearance energies for four amines. A 298 K heat of formation of 749.5 ± 1.3 kJ/mol is derived for $CH_2NH_2^+$, leading to an absolute proton affinity of 868.8 ± 2.5 kJ/mol for methylenimine [2]. The 298 K heat of formation for $CH_3CHNH_2^+$ is determined to be 665.0 ± 1.4 kJ/mol, resulting in an absolute proton affinity for ethylidenimine of 907.3 ± 3.6 kJ/mol.

High level *ab initio* calculations were performed for each unimolecular reaction and energy profiles determined. Those precursors that showed a reverse activation barrier were not included in the final estimations of $\Delta H_{f,298}(XCHNH_2^+)$. All experimental values were compared with the theoretical calculations to validate the accuracies of the derived cationic heats of formation.

1. M. Meot-Ner (Mautner), "The proton affinity scale, and the effects of ion structure and solvation." *Int. J. Mass Spectrom.* **227**, 525 (2003).

2. Z. A. Harvey and J. C. Traeger, "Heat of formation for the methylenimmonium cation by photoionization mass spectrometry." *Europ. J. Mass. Spectrom.* In Press.