The Propionyl Cation Heat of Formation Revisited

Zoë A. Harvey and John C. Traeger

Department of Chemistry, La Trobe University, Victoria 3086.

The 298 K heat of formation for the propionyl cation ($C_2H_5CO^+$) has been measured previously by dissociative photoionization mass spectrometry [1]. On the basis of appearance energy measurements for a range of precursors, a value of 591.2 ± 2.3 kJ/mol was derived. This has been used as the recommended value in the extensive GIANT thermochemical compilation [2] and as a reference point for the absolute proton affinity for methylketene [3]. However, recent theoretical and experimental studies involving methylketene suggest that the above $\Delta H_f(C_2H_5CO^+)$ has been significantly underestimated [4-7], resulting in a methylketene proton affinity that is too high by ~30 kJ/mol [8].

In this study, the previous appearance energies [1] have been carefully re-evaluated, with various possible sources of error being investigated. As a result, it is found that only 2-butanone provides a suitable precursor molecule whose appearance energy can be used to determine a reliable propionyl cation heat of formation.

From the *m/z* 57 appearance energy of 10.199 ± 0.003 eV for 2-butanone measured here, a value of 617.7 ± 1.0 kJ/mol is derived for $\Delta H_f(C_2H_5CO^+)$ at 298 K, which corresponds to 845.5 ± 4.8 kJ/mol for the proton affinity of methylketene. These experimental results are supported by high-level *ab initio* molecular orbital calculations.

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