THE ABSOLUTE PROTON AFFINITY FOR METHYLKETENE

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Most gas-phase proton affinities (PAs) are obtained from experiments involving measurements on a relative scale. An absolute PA can only be established when the heats of formation for both a given molecule and its protonated counterpart are well known. In their extensive compilation, Hunter and Lias[1] selected a value of 834.1 kJ/mol for the PA of methylketene. This was based on an estimate[2] of –104.6 kJ/mol for the neutral methylketene heat of formation and an experimental measurement of 591.2 kJ/mol for $_{r}H_{f}$ ($C_3H_5O^+$).[3] However, $_{r}\Delta_{f}$ (methylketene) has been shown to be significantly higher, with high-level theoretical calculations[4,5] being in good agreement with a derived experimental value of –66.9 kJ/mol.[6] This would then lead to a PA for methylketene of 871.9 kJ/mol, a value which is ~30 kJ/mol higher than both a recent experimental thermokinetic measurement of 842 kJ/mol [7] and a corresponding theoretical calculation of 843 kJ/mol.[5] The present study aims to resolve this apparent discrepancy by a careful re-evaluation of the 298 K heat of formation for the propionyl cation. Threshold photoionization mass spectrometry has been used to measure appearance energies for the formation of $C_3H_5O^+$ from several different precursors. On the basis of these, it is proposed that the propionyl cation heat of formation should be revised upward to 618.4 kJ/mol, which corresponds to an absolute PA for methylketene of 844.7 kJ/mol.

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