Gas Phase Enthalpy of Formation of the 1-Acetylvinyl P-Nitrobenzoate

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The captodative olefins as the 1-acetylvinyl p-nitrobenzoate have an important role in the Diels-Alder reactions; this is due to the opposite electronic effect displayed by their geminally substituted functional groups, being then very efficient synthons in the synthesis of terpenoids. Thermochemical properties of these types of molecules are currently unknown, for this reason in the present work we report the first measurements of the enthalpies of combustion, formation and sublimation of this substance.

An isoperibolic micro-bomb combustion calorimeter was utilized to quantify the energy of combustion of this olefin. The apparatus was previously tested by measuring the standard molar enthalpy of combustion of a secondary standard as the acetanilide, founding for this substance a value of -(4222.5 ±1.1) kJ/mol, which is in very good agreement with the recommended one. Once the accuracy of the device corroborated, using samples of around 25 mg of the 1-acetylvinyl p-nitrobenzoate per experiment of combustion, we derived from the experimental results a value of -(5147.9 ±5.5) kJ/mol for the enthalpy of combustion of this compound, calculating then its standard enthalpy of formation as -(467.0 ±5.6) kJ/mol.

On the other hand, to quantify the enthalpy of sublimation we have used a quartz crystal microbalance, determining the rate of effusion at different temperatures and, applying a combination of the Knudsen equation for the substance's vapor pressure and the Clausius–Clapeyron equation for its corresponding dependence with the temperature, the enthalpy of sublimation determined in this way is (126.4 ±2.2) kJ/mol. Adding this value to the standard enthalpy of formation, the resulting gas phase enthalpy of formation is –(340.6 ±6.1) kJ/mol. The value computed by a group contribution method leads to the result –365.1 kJ/mol, which means a difference less than 7.3% respect to the experimental one.