Theoretical thermochemistry: *ab initio* heat of formation for hydroxylamine

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**ABSTRACT**

Theoretical methods are necessary to predict thermodynamic values for chemicals when sufficient experimental data or reliable estimations are not available. Hydroxylamine (HA) is an example of a highly reactive and poorly characterized compound with important industrial applications. In this work, the heat of formation for gaseous hydroxylamine is calculated, under standard conditions, using isodesmic reactions at several levels of theories, including HF, B3P86, B3LYP, MP2, MP3, MP4, CCSD(T), G2, G2MP2B3, G3B3, G3, and CBS-Q, and several basis sets, including Dunning correlation consistent and Pople-style. To gauge the computed HA values, the gaseous hydrogen peroxide heat of formation is calculated by the same methods and compared with experimental data. Also, for comparison with a traditional empirical approach, the HA heat of formation is calculated by the Benson group contribution method.

Based on our calculations we recommend an average value of -11.4 kcal/mol for the gaseous HA heat of formation at 1 atm and 298.17 K. The mean average deviation relative to the experimental values for the methods employed is approximately 1.1 kcal/mol. These results provide guidance for selecting levels of theory and basis sets for obtaining thermochemical values, which are important for the design of safe and economical chemical processes.