

A Shock Tube Study of the Enthalpy of Formation of OH

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Overview

The standard enthalpy of formation of the hydroxyl radical (OH) at 298K, $D_fH^\circ_{298}(\text{OH})$, has been determined from shock tube measurements spanning the temperature range 1964K to 2718K and at pressures of 1 to 2.4 atm. Low concentration, lean and stoichiometric mixtures of H₂ and O₂ in Ar produce well-controlled levels of OH in a “partial equilibrium” state, with little or no sensitivity to the reaction kinetics. The partial equilibrium OH concentrations are dependent only on the thermochemical parameters of the reacting species, with the heat of formation of OH being the most significant and uncertain parameter.

Narrow-linewidth UV laser absorption at 306.7nm is used to measure OH concentrations with sufficient accuracy (2-4%) to clearly determine the value of the enthalpy of formation. Over the whole range of experimental conditions, the average determination is $D_fH^\circ_{298}(\text{OH}) = 8.92 \pm 0.16$ kcal/mol (37.3 ± 0.67 kJ/mol) with a standard deviation of $s = 0.04$ kcal/mol (0.17 kJ/mol). This value is 0.40 to 0.48 kcal/mol (1.7 to 2.0 kJ/mol) below the previously accepted values, and agrees with recent theoretical calculations, experimental studies using the positive-ion cycle, and calculations using thermochemical cycles.

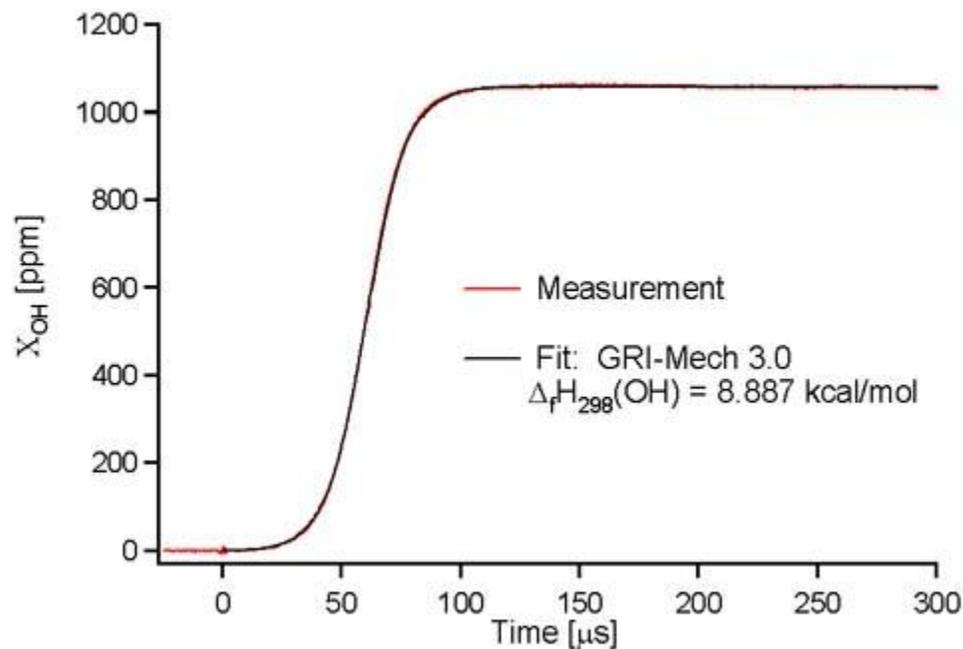


Figure 1: Experimentally measured and modeled OH mole fraction time-histories. Conditions are $T_5 = 2590$ K, $P_5 = 1.075$ atm, and the mixture is 4002 ppm H₂ / 3999 ppm O₂ / balance Ar. The OH concentration is modeled using GRI-Mech3.0 and the GRI-Mech3.0 thermodynamics database, with 0.5ppm additional H-atoms to match the induction time. The fit required a change in $D_fH^\circ_{298}(\text{OH})$ from 9.403 to 8.887 kcal/mol.

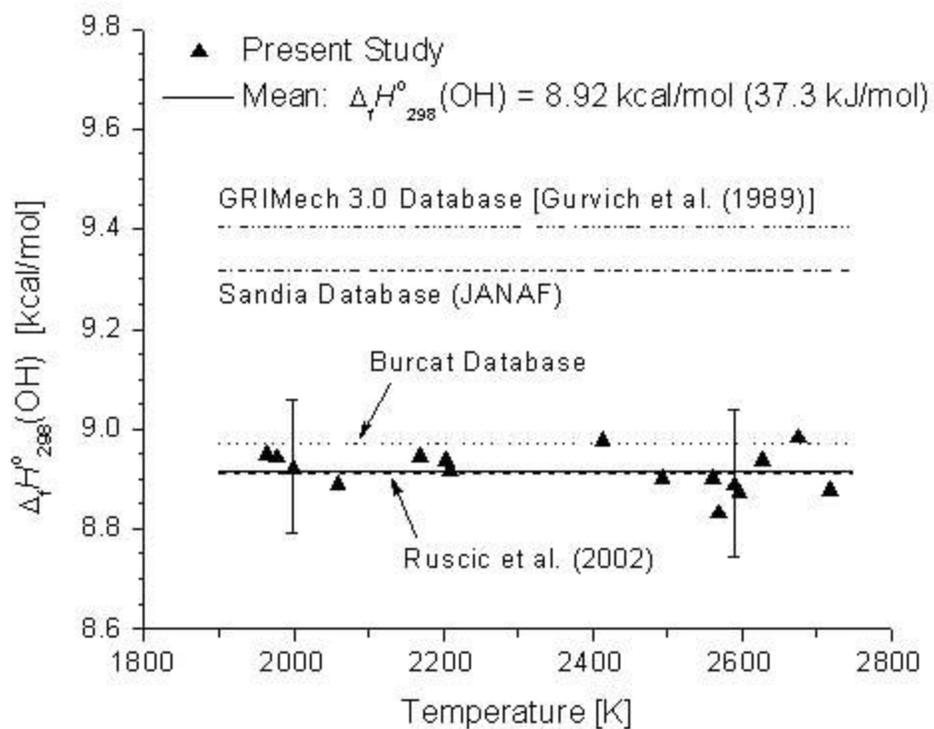


Figure 2: Experimentally derived values for $\Delta_f H^\circ_{298}(\text{OH})$. Standard deviation from the mean is $s = 0.04$. Previous values are given for reference.

References

1. J.T. Herbon, R.K. Hanson, D.M. Golden, and C.T. Bowman, "A shock tube study of the enthalpy of formation of OH," 29th Int. Symp. on Combustion Proc. of the Comb. Inst. 29 1201-1208 (2002).