

PHOTOIONIZATION OF HOCO RADICAL: A NEW UPPER LIMIT TO THE ADIABATIC IONIZATION ENERGY AND LOWER LIMIT TO THE ENTHALPY OF FORMATION

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HOCO radical is important in combustion and atmospheric chemistry. A recent photoionization investigation provides a new value for the adiabatic ionization energy of $\text{EI}(\text{t-HOCO}) \leq 8.195 \pm 0.022$ eV. Through the positive ion thermochemical cycle, this translates into a lower limit to the enthalpy of formation, $\Delta H_{f0}^{\circ}(\text{t-HOCO}) \geq -45.8 \pm 0.7$ kcal/mol ($\geq -46.5 \pm 0.7$ kcal/mol at 298 K), placing t-HOCO only 3.5 ± 0.7 kcal/mol below the $\text{CO}_2 + \text{H}$ asymptote. The photoionization spectrum of HOCO corroborates the previous finding of a progression in the double C=O bond stretch of the ion of ~ 2300 cm^{-1} , suggests the presence of the single C-O bond stretch of ~ 1200 - 1300 cm^{-1} , and provides indirect evidence for the excitation of an even lower frequency, such as the OCO bend. In addition, the data tentatively suggest an ionization onset as low as 8.06 ± 0.03 eV. While it is not quite clear whether the latter should correspond to the cis or trans isomer, it may indicate that the enthalpy of formation of HOCO is even higher. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under Contract No. W-31-109-ENG-38.