Probing the OH + CO → H + CO_2 reaction by dissociative photodetachment of $HOCO^-$ anions in a cryogenic ion trap

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As a fundamental elementary chemical reaction, OH + CO → H + CO_2 has been the subject of extensive study. However, significant questions remain regarding the microscopic mechanism at play, particularly about the role of H-atom tunneling in the product channel, due to difficulties in isolating and probing the HOCO intermediate. Photoelectron-photofragment coincidence (PPC) experiments have provided direct insights into the nature of the potential energy surface (PES) governing this reaction but have been obscured by the presence of internal excitation in these precursor anions. In these experiments, a dissociative neutral of known internal energy is prepared by photodetachment of an anionic precursor, and all neutral products are detected in coincidence with this photoelectron for a kinematically complete measurement. A new instrument incorporating a cryogenically cooled electrostatic ion beam trap[1] has alleviated issues of anion internal excitation by allowing PPC spectroscopy to be performed on cold anions that remain stored for several seconds in a cryogenic environment. Using this instrument, the presence of tunneling is confirmed on the HOCO potential energy surface.[2] The increased accuracy and resolution resulting from cold anions allows for a reassignment of the electron affinities of the cis- and trans- isomers of the HOCO intermediate in vibrationally-resolved photoelectron spectra. This also has allowed for direct extraction of a model 1-D barrier governing dissociation to H + CO_2 from experimental tunneling lifetimes.[3] This instrument provides new opportunities for extension of the PPC technique by pumping of precursor anions vibrational modes prior to photodetachment or controlling the isomer population in the ion beam.

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References

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