The OH + CO Reaction System: *ab initio* SCTST Rate Constants and Semi-Empirical Master Equation Models

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The OH + CO reaction system is of great importance both in combustion and in the atmosphere. It has also become a benchmark for kinetics, dynamics, and electronic structure calculations.[1] It is convenient for this purpose because all of the individual reaction steps have intrinsic energy barriers (the problems associated with barrier-less reactions can be avoided), isomerization reactions occur, quantum mechanical tunneling is important, and pre-reactive complexes are present, some of which involve hydrogen bonding. In other words, it is a microcosm that contains many of the features found in much larger reaction systems.

We will describe our calculations using Semi-Classical Transition State Theory (SCTST),[1] which was originally developed by W. H. Miller and colleagues,[2] as implemented by some of us[3] and distributed as part of the MultiWell package.[4] Harmonic vibrational frequencies, vibrational anharmonicities, and rotational constants were calculated using the highly accurate CCSD(T) level of theory with large basis sets, as implemented in CFOUR.[5] Another key feature is that relative energies were computed using the *ab inito* HEAT-345Q protocol,[6] which is known to produce energies better than 1 kJ mol^{-1}. For the master equation calculations, the parameters associated with collision frequency and energy transfer were estimated and adjusted to give reasonable agreement with the pressure effects observed in experiment near 300 K. The resulting semi-empirical master equation model calculations, carried out using the MultiWell package,[3] are in good agreement with the pressure-dependent experimental data at $T \geq 300$ K. At $T < 300$ K, the accuracy decreases from semi-quantitative to qualitative, probably as a result of small errors in the *ab initio* energies and other factors, as will be discussed.

References

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(6) See Ref. 1 for literature citations.