

**Catalysis by cationic oxorhenium(V): Hydrolysis and alcoholysis of organic silanes**

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**Electronic Supplementary Information:** S1 Schematic figure of RGA-MS (including description of general instrument design elements and customizations undertaken to ensure amenability towards kinetic experiments); S2 figure illustrating rate correlation ( $\log k_1$ ) with the relative Si-H bond energy; S3 figure illustrating electronic ( $\sigma^*$ ) LFER correlation.

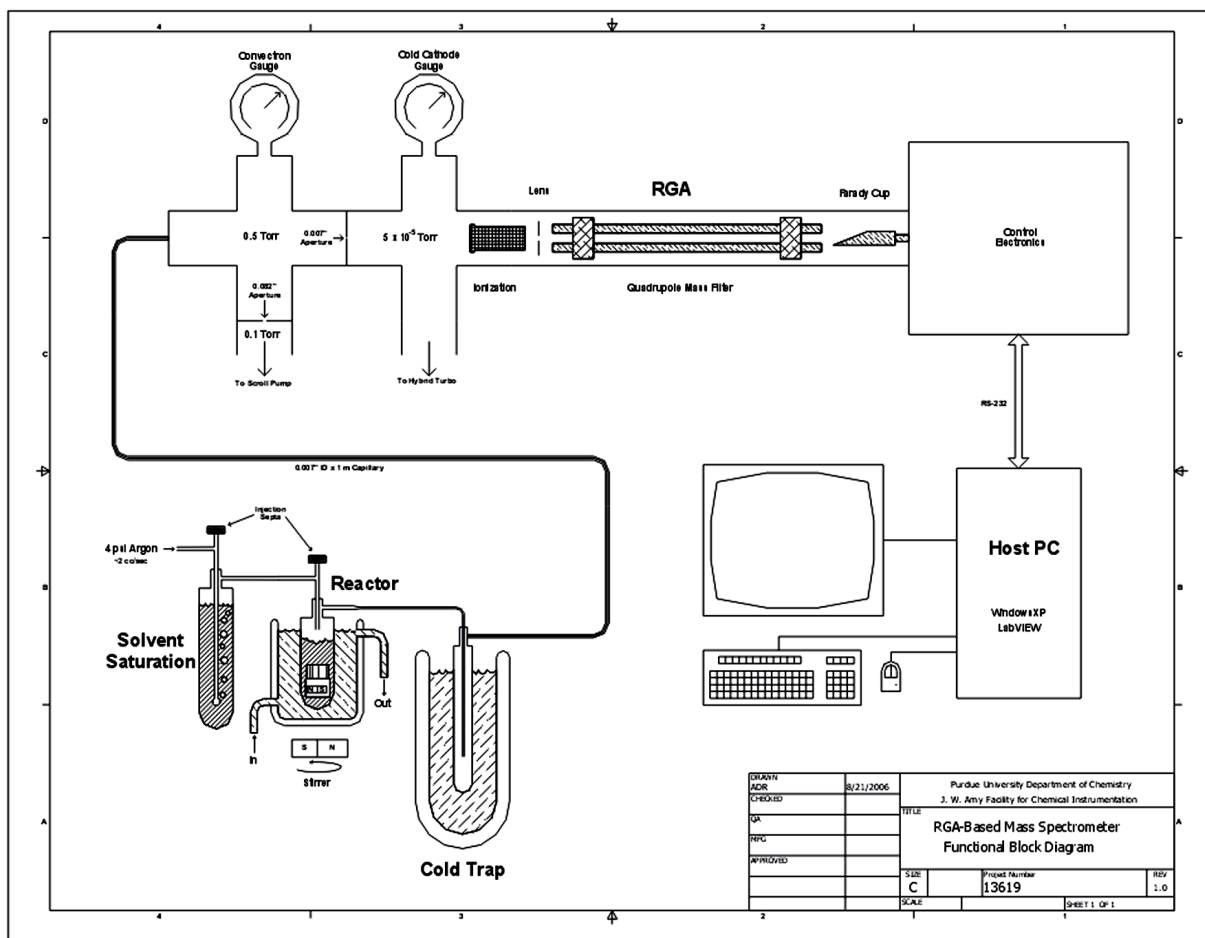


Figure S1. Schematic drawing of customized RGA-MS mass spectrometer setup. The RGA-MS is a commercially available Stanford Research Systems instrument (model RGA100). The mass spectrometer relies upon an electron impact ionization method with a quadrupole mass filter system and a Faraday Cup detector. The RGA is capable of monitoring any small molecule fragments ranging from 1-100 amu with sufficient resolution for 1 amu differentiation. Compressed Ar is used as an inert carrier gas and is regulated to approximately 4psi (over atmospheric pressure) and proceeds with  $\approx 2\text{cm}^3\text{min}^{-1}$  flow rate throughout the system. A customized sample introduction system with means for temperature control, efficient mixing, and inhibition of solvent evaporation make this system amenable for kinetic experiments. To ensure consistency in reaction solution volume, the carrier gas is pre-saturated by bubbling through the solvent used (solvent saturation chamber) prior to entering the reactor. The reactor is equipped with a magnetic stirring bar to ensure efficient gas evolution from the reaction solution into the reactor head space. To regulate the reaction solution temperature, the reactor is submerged into a temperature controlled ethylene glycol bath held in a jacketed glass vessel with circulating ethylene glycol regulated by a VWR model 1140S immersion circulating bath with digital temperature control.

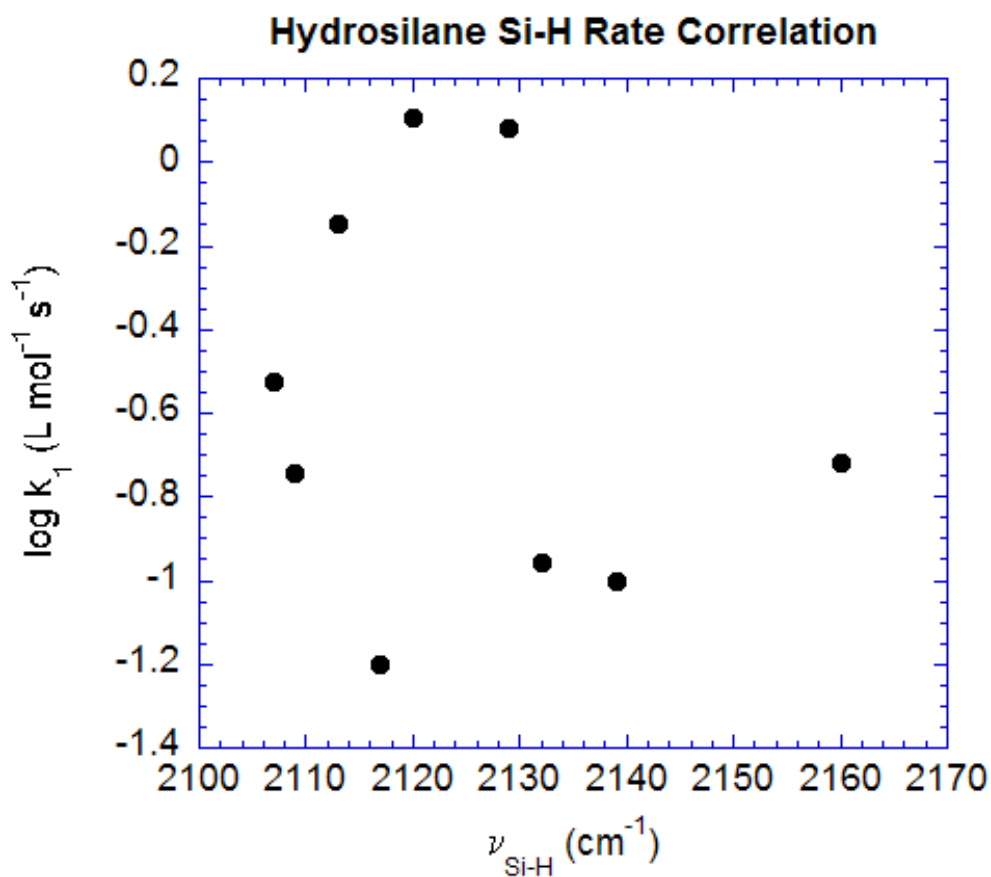


Figure S2 Plot illustrating rate correlation ( $\log k_1$ ) with relative Si-H bond energy ( $\nu_{\text{Si-H}}$ ) for the complex 1 catalyzed hydrolysis reaction of organosilanes (entered in Table 2). The Si-H stretching frequencies were used to provide a relative representation of the electronic variations in the Si-H bond strengths, substituting for Si-H bond disassociation enthalpy values (which are not readily available for the substrates studied).

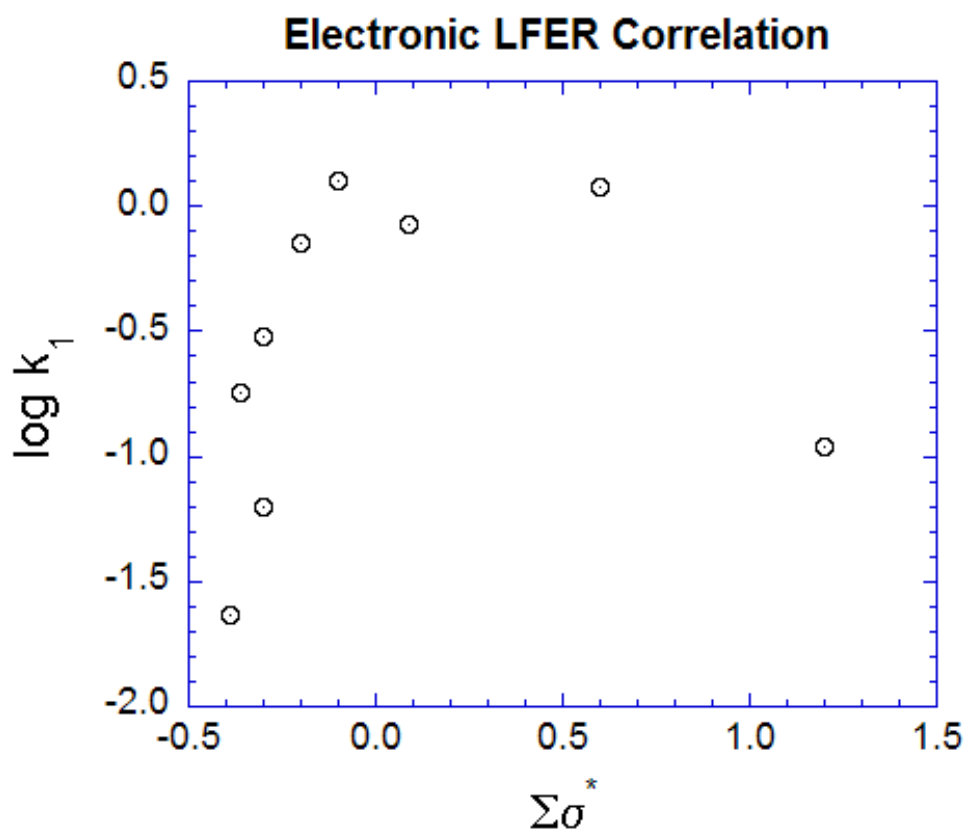


Figure S3 Plot illustrating the electronic  $\Sigma\sigma^*$  (representative of the complete  $\text{SiR}_4$  electronic environment) LFER correlation. This Taft polar energy plot, for the complex 1 catalyzed hydrolysis reaction of organosilanes, reflects the substituent induced electronic effects upon the silicon center.