

281h A Theoretical Kinetic Investigation of Arsenic and Selenium in Combustion Flue Gases

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Coal power, a well tested and reliable energy source, is the leading energy producer in the United States; in fact, over half of the electricity generated in the US is derived from the combustion of coal. It does, however, have its drawbacks, most notably the emissions it gives off. These emissions are mostly carbon monoxide and dioxide as well as NO_x and SO_x, but they also contain a variety of species composed of trace metals such as mercury, arsenic, and selenium. The focus of this study has been upon arsenic and selenium due to the lack of knowledge present in the literature. Because certain species of these elements are harmful to the environment and toxic to humans, the need to remove these compounds before they enter the atmosphere is paramount. However, the design of efficient removal processes is hampered by a lack of knowledge about exactly which species compose the flue gas after the combustion process. To determine the speciation of these elements it is necessary to first go back and examine the kinetics of the interactions which form them to get a better idea of exactly what is taking place in that environment. With this in mind, the objective of this study is the determination of the rate constants and activation energies of the various interactions which occur, using computational chemistry. Ab initio methods are used to calculate optimized geometries, frequencies, and reaction enthalpies, and these are compared to experiment. All calculations have been performed using the Gaussian98/Gaussian03 software package at several different levels of theory including the methods QCISD(T) and CCSD(T), the complete Pople basis set 6-311++G(3df,3pd) and the Effective Core Potentials Stuttgart and SBK. Those levels of theory which most closely approximated experimental data were then used in the further development of potential energy surfaces (PES). After validating the theoretical models by comparison to available experimental data, the energetics data collected at varying temperatures was used to develop the PES's from which the activation energy could be determined. The pre-exponential component of the rate constant was found using Transition State Theory (TST) and Rice, Ramsperger, Kassel, and Marcus (RRKM) Theory; TST for bimolecular reactions and RRKM for unimolecular reactions. Combining both the pre-exponential factor and activation energy allowed the kinetic rate constant to be determined for several reactions.