Application of Computational Chemistry to the Aqueous-Phase Oxidation of Hydroxylamine by Nitric and Nitrous Acids

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The Plutonium-Uranium Reduction Extraction (PUREX) process is used to convert nuclear waste materials into a mixed-oxide fuel suitable for use in civilian power plants. An important step in this process is the aqueous-organic extraction that separates plutonium and uranium, using hydroxylamine (NH_2OH) as a reducing agent. The aqueous phase is a nitric acid ($HONO_2$)/hydroxylamine solution, with nitrous acid (HONO) being an important impurity. This solution can undergo an autocatalytic reaction between hydroxylamine, nitric acid, and nitrous acid that results in excess HONO formation, feeding the autocatalytic cycle. A competing scavenging reaction of NH_2OH with HONO tends to stabilize the system by converting the hydroxylamine and nitrous acid into nitrous oxide (N_2O). There are potential side reactions with other impurities, such as dissolved oxygen which may be important to accurately describe system behavior. The combination of the autocatalytic and scavenging reactions can result in the production of heat and gases that cause pressure buildup and potentially vessel rupture. This is a major concern when radioactive substances coexist with this mixture, and there have been seven incidents in the U.S. that have been attributed to this autocatalytic phenomenon.

The goal of this research was to apply modern computational chemistry techniques to the aqueous phase system in an attempt to better understand the system dynamics and more confidently predict behavior outside the narrow range of experimental data. This sort of predictive chemical kinetics approach has been very helpful for understanding comparably complex autocatalytic gas-phase processes, e.g. fuel ignition. However, the present work is one of the first attempts to extend predictive kinetics to a complex series of unknown reactions with strong solvent effects. The project involved developing a method to better predict the thermochemistry and rate parameters of species in solution, and constructing a detailed model to describe the system. It also required an investigation of exactly what influence the solute-solvent interactions have on the thermochemistry and kinetics. Previously proposed kinetic models of the system were very simplistic and adjusted to fit the narrow range of experimental data. The model presented here is an elementary mechanism (45 species and 80 reactions) that combines the limited amount of experimental thermochemical data with computational chemistry estimates of thermochemical and rate parameters.

The methodology used for estimating the thermochemistry requires a multi-step process. First, an accurate gas-phase estimate of the enthalpy of formation is obtained using a high level compound method, CBS-QB3 in this case. Empirical bond additivity corrections were also included in the gas phase to further refine the estimates. A lower level DFT estimate of the energies in solution was obtained using the IEFPCM continuum solvation model of Gaussian03 (G03), which was combined with an equivalent level gas-phase calculation to yield an estimate of the solvation free

energy of the molecule. The free energy of solvation can be converted to an enthalpy of solvation when combined with the entropy of solvation. The solvation entropy was calculated through a combined approach with both theoretical and empirical components. Pieriotti's formula for the free energy of cavitation was used to predict the solvation entropy assuming the solvent radius is 1.35 angstroms. An empirical portion based on the solute bonds that interact with the solvent was also included, and fit to the limited amount of experimental entropy data available for this system. The solute radius was taken as the spherically-equivalent radius to the volume predicted by G03, with a constant empirical correction added to all radii. This factor is typically between -15 and -30 cal/mole-K for small molecules in water, which becomes especially important in non-eqimolar reactions. The enthalpy of solvation could then be determined from the solvation free energy and entropy, which was combined with the gas phase heat of formation to yield a base estimate of the solution phase heat of formation. Solution phase bond additivity corrections were also included to refine the solution phase thermochemistry based on available experimental data.

Transition state theory (TST) rate constant estimates were based on the traditional gas-phase equations, using solution-phase ab initio estimates of partition functions and barriers. The barriers employed implicitly include the solvation free energy, which in theory corrects the gas phase TST estimate to a solution phase estimate. Activity coefficients may also have an effect, but were ignored due to the unreliability of transition state activity coefficient estimates.

$$k_{TST} = \frac{k_B T}{h} \cdot C_0^{-\Delta N_{TS}} \cdot \frac{Q^{TS}}{Q_A Q_B} \cdot \exp\left[\frac{-E_0(0K)}{RT}\right] \cdot \frac{\gamma_{R1} \cdot \gamma_{R2}}{\gamma^\dagger}$$

These TST estimates likely have significant errors stemming from quantum mechanical approximations, the grossly simplified polarizable continuum solvation model, and typical uncertainties that are involved in gas-phase TS calculations. Fortunately, many of the reactions are diffusion-limited, making the estimates of those rates much more accurate than the reactions with significant, solvent-dependent barriers.

A detailed chemical kinetic model was constructed based on previously postulated mechanisms and an exhaustive computational scan of potential reactions. The estimated thermochemistry used in the model was modified to match dilute, experimental pK_A values reported for HONO, $HONO_2$, and NH_3OH^+. With small modifications to species thermochemistry and rate constants, the model is able to reproduce experimental HONO yield data at acid concentrations below 3M well. In order to achieve agreement in more concentrated acid solution, the experimentally-determined activity coefficients of the major species (H_2O, $HONO_2$, H_3O^+, and NO_3^-) must also be built into the model. When including the non-idealities of the major species, a qualitative yield agreement was seen over a large range of nitric acid, hydroxylamine, and nitrous acid concentrations. Without any modifications, one major problem with this model was that the predicted ignition time, defined as the time at which the inflection point occurred in the HONO trace, was several orders of magnitude too large, signifying significant errors in either rate

constants or thermochemistry. It is believed that errors in the TST rate constant were the main cause of this discrepancy, but that errors in thermochemistry also contribute to this error. A yield and ignition time sensitivity analysis was performed with respect to both rate constants and thermochemistry, which revealed the parameters most influential to the system. These parameters were the ones modified to achieve the near-quantitative agreement with both yield and ignition time experimental data.

The sensitivity analysis and accompanying flux analysis was able to predict the autocatalytic and scavenging pathways, based on the thermochemistry and rate constant estimated here. The results are somewhat different than what is currently proposed in the literature, though the significant uncertainties also translate to uncertainties in the reaction pathways. The pathway traditionally believed to occur in the autocatalytic reaction results in NH_2OH reacting with N_2O_4 (or some form thereof), resulting in HNO, which is further convert to N_2O_3 and finally, HONO. This work differs in the initial part of the pathway, but is similar in the later steps after HNO is consumed. The initial reactions leading into the scavenging and autocatalytic pathways:

$$H_3O^+ + HONO \xrightleftharpoons{Diffusion} NO^+ + 2H_2O$$
$$NH_3OH^+ + NO^+ + H_2O \rightleftharpoons NH_3ONO^+ + H_3O^+$$
$$NH_3ONO^+ + H_2O \xrightleftharpoons{Diffusion} H_3O^+ + NH_2ONO$$
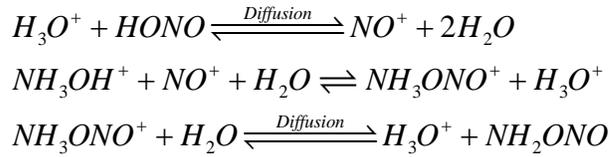
Following the formation of NH_2ONO, the autocatalytic pathway proceeds through the following steps:

$$NH_2ONO \xrightleftharpoons{Diffusion} NH_2O^\bullet + NO^\bullet$$
$$NO_2^\bullet + NH_2O^\bullet \rightleftharpoons HONO + HNO$$
$$HNO + NH_2O^\bullet \rightleftharpoons NH_2OH + NO^\bullet$$
$$NO^\bullet + NO_2^\bullet \xrightleftharpoons{Diffusion} ONONO$$
$$ONONO + H_2O \rightleftharpoons 2HONO$$
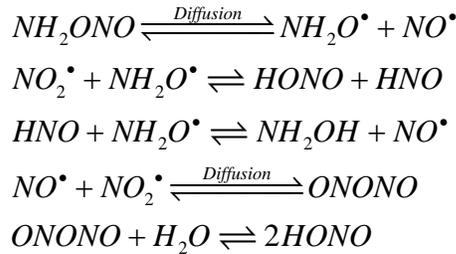
With important supplementary reactions being the following, which serve to produce the NO_2 radicals used in the H-abstraction reactions:

$$NO^+ + NO_3^- \xrightleftharpoons{Diffusion} ONONO_2$$
$$ONONO_2 + H_2O \rightleftharpoons HONO + HONO_2$$
$$ONONO_2 \xrightleftharpoons{Diffusion} NO_2^\bullet + NO_2^\bullet$$
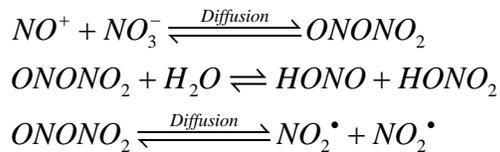
The scavenging pathway proceeds in much the way previously proposed in the literature, with the following steps:

$$NH_2ONO \rightleftharpoons ONNH_2O$$

$$H_3O^+ + ONNH_2O \xrightleftharpoons{Diffusion} ONNH_2OH^+ + H_2O$$

$$ONNH_2OH^+ + H_2O \xrightleftharpoons{Diffusion} H_3O^+ + ONNHOH$$

$$ONNHOH + H_3O^+ \xrightleftharpoons{Diffusion} ONNH^+ + 2H_2O$$

$$ONNH^+ + H_2O \xrightleftharpoons{Diffusion} N_2O + H_3O^+$$
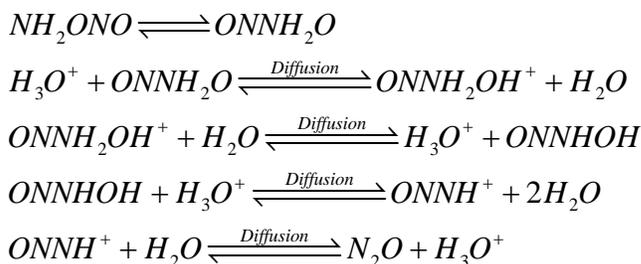
The figure below shows some representative results from the modeling effort, compared with experimental yield or induction time data. The trends in the HONO yields and HONO absorbance traces produced by the model are in good agreement with the data.
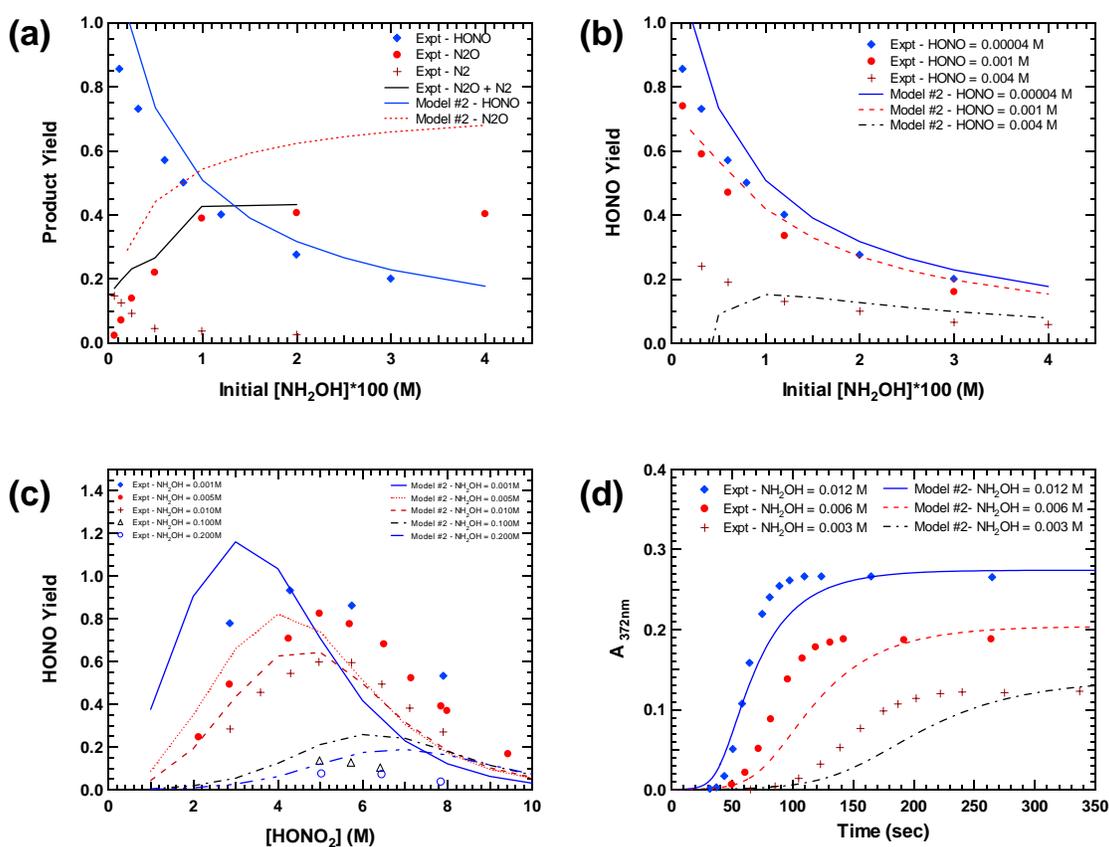
Figure 1: Comparison of modified model predictions with experimental yield and ignition time data. (a) & (b) Product yield data as a function of initial NH$_2$OH concentration. (c) HONO yield as a function of nitric acid concentration. (d) Absorbance at 372 nm (HONO) as a function time showing the ignition time characteristics for various initial conditions. (a), (b), and (d) experimental data from: Bennett et al, *Inorg. Chem.* 1982, 2461. (c) experimental data from: Pembridge and Stedman, *J. Chem. Soc. Dalton*, 1979, 1657.

One major problem persists with the model, its inability to predict system stability, where the initial charge of HONO would be completely consumed in the scavenging reaction. The result would be very little NH$_2$OH consumed, and a HONO concentration that is driven to zero. This is

seen experimentally at low temperatures, but is not predicted by the current model. There could be a number of causes of this deficiency, including missing reactions and/or incorrect temperature dependences of the rate constants. The stable system likely arises because the scavenging-to-autocatalytic rate ratio increases or from a side reaction that drives HONO to zero, but which only becomes important at lower temperatures. The stability could arise from the autocatalytic pathway being more temperature dependent than the scavenging, meaning that the generation rate of HONO would slow more quickly than the consumption rate with decreasing temperature.

The methodology outlined here can play an important role in understanding the reaction mechanisms of complex aqueous phase processes. At present, significant errors in the estimation techniques, quantum mechanical calculations, and solvation models make the ab initio model predictions significantly uncertain. The fact that the system is near room temperature only serves to exacerbate the estimation errors, as errors of ~1.4 kcal/mole in activation barriers or ΔG_{Rxn} results in order of magnitude changes in rate and equilibrium constants. However, it was seen that in the complex example system investigated, modest modifications to the system parameters can yield good agreement with experimental data. This fundamentally-based modeling approach potentially allows more confident extrapolation to operating conditions that have not been probed experimentally, and can provide additional insight into system dynamics. It is hoped that the present study will encourage the development of more accurate, practical methods for estimating energies and entropies of solvation needed for accurate modeling in condensed phases.