

Developing a Kinetic Model for the Evolution of Hydrogen Gas from Photolyzed Benzene

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Abstract:

A kinetic model for the rate of appearance of Hydrogen gas from photolyzed Benzene is successfully developed from first principle methods and a Lindemann kinetic mechanism. The model is curve-fit with empirical data and shown to be in good agreement with observed H₂ evolution rates. Collision theory is used to estimate the frequency of encounter pair interactions in solution and suggests that diffusion of these radicals is the rate limiting step for the reaction. It is suggested that the rate of evolution of H₂ is independent of initial concentration of Benzene precursor for sufficiently large initial concentrations, and this assumption is the basis for the formation of the model presented in this paper.

Introduction:

The photolysis mechanism of Benzene is regarded to be either a one or two photon absorption process whereby excited electronic states decay via radiationless internal conversion to S_0 ^[1]. This produces a vibrationally active “hot” Benzene and stipulates that all photo-reactants are produced from the ground state potential energy surface. A conical intersection between S_1 and S_0 has been shown to exist in the Benzene molecule which allows a non-adiabatic electronic transition to take place due to a breakdown of the Born-Oppenheimer approximation^[3]. DFT calculations predict that one photon absorption stimulates molecular Hydrogen loss with an exit barrier of ≈ 507 kJ/mol, and that the two photon absorption mechanism first produces a methylene-bridge intermediate with a ≈ 374 kJ/mol barrier followed by either molecular or atomic Hydrogen emission again at ≈ 507 kJ/mol^[1]. It was suggested in previous work that the internal conversion of electronic excited states to “hot” Benzene stimulates vibrational modes corresponding to C-H stretches, and that it is the volatility of these vibrations which are responsible for C-H homolysis^[4]. Calculations of vibrational temperature from calculated and experimental specific heat capacity were shown to be commensurate with observed C-H stretch modes in Benzene^[5].

This work now seeks to describe the rate at which molecular Hydrogen evolution occurs. A first order rate constant corresponding to the rate of C-H homolysis is calculated and is in good comparison with experimental data; however, this rate constant does not accurately describe the evolution of H_2 . Thinking about the reaction, it is fairly clear that the formation of H_2 from Hydrogen radicals is contingent upon the diffusion of encounter pairs in solution. Thus, this is a good explanation for why the photolytic rate constant does not describe observed data. This paper begins by calculating said rate constant and showing the solution to the first order rate equation. From this rate, a Lindemann mechanism is constructed and used to produce the final model in this paper.

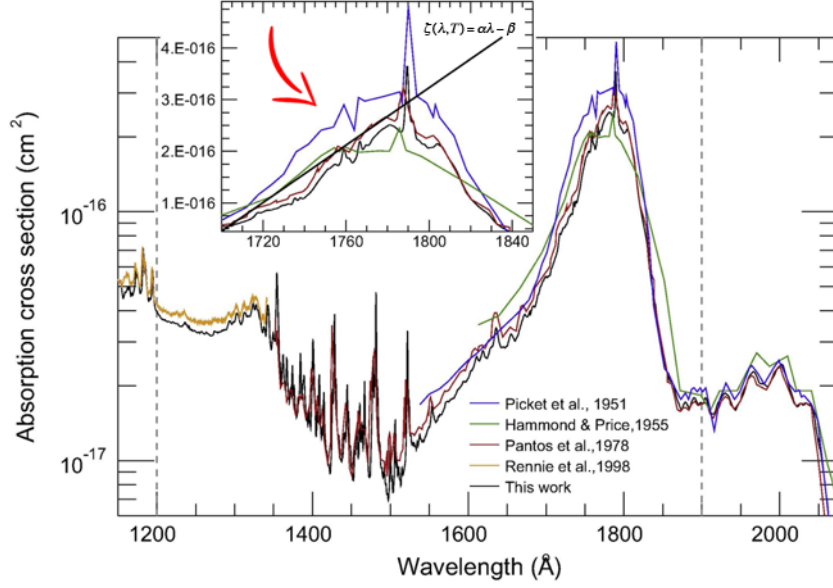
Construction of a Model:

Eq 1. The photolysis rate constant is defined as the following, where $\zeta(\lambda, T)$ is the absorption cross section as a function of incident wavelength and temperature, $\phi(\lambda, T)$ is the quantum yield, $F(\lambda, T)$ is photon flux, and the upper and lower limits of integration define the domain over which the integrand is valid^[2],

$$J = \int_{\lambda_1}^{\lambda_2} \zeta(\lambda, T) \phi(\lambda, T) F(\lambda, T) d\lambda$$

Eq 2. Using data taken from the following graph, the absorption cross section of Benzene is modelled linearly as the following where α & β are constants;

$$\zeta(\lambda, T) = \alpha\lambda - \beta$$



Data courtesy of;

Capalbo, Fernando J, et al. "New Benzene Absorption Cross Sections in the VUV, Relevance for Titan's Upper Atmosphere." *Icarus*, vol. 265, Feb. 2016, pp. 95–109.

Eq 3. The quantum yield is a heavyside function of λ corresponding to either a one or two photon absorption photolysis mechanism ^[1];

$$\phi(\lambda, T) = \frac{1}{2}(1 + u_{193}(\lambda))$$

Eq 4. And the photon flux is estimated from the documented power density of the plasma lamp used in the experiment ($\approx 15 \text{ mW/cm}^2$). Here, let the number of emitted photons per square centimeter, n_p , be related to power density, E , as follows;

$$\bar{E} = \frac{n_p hc}{\lambda} \rightarrow n_p = \frac{\bar{E} \lambda}{hc}$$

$$F(\lambda, \theta) = n_p = \frac{\bar{E} \lambda}{hc}$$

Eq 5. Therefore, the photolytic rate constant J is estimated as follows;

$$J = \int_{\lambda_1}^{\lambda_2} \frac{\bar{E} \lambda}{2hc} (\alpha \lambda - \beta) (1 + u_{193}(\lambda)) d\lambda$$

$$J = \frac{(1 + u_{193}(\lambda))\bar{E}\lambda}{2hc} \left(\frac{\alpha\lambda^3}{3} - \frac{\beta\lambda^2}{2} \right)_{\lambda_1=172nm}^{\lambda_2=179nm}$$

$$8.2 * 10^9 s^{-1} < J < 1.6 * 10^{10} s^{-1}$$

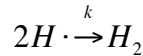
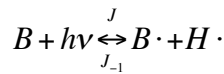
Eq 6. If J is taken to be the rate constant describing the rate of evolution of Hydrogen gas, then the following is deduced;

$$\frac{dH_2(t)}{dt} \approx -\frac{dB(t)}{dt} = -JB(t)$$

$$\ln|B(t)| = -Jt + c : B(0) = B_0$$

$$B(t) = B_0 e^{-Jt}$$

Eq 7. It is clear from empirical data that a simple first order rate constant relationship (with J) is not sufficient to describe the reaction mechanism. For all graphical representation purposes, the function B(t) described in Eq 6 approximates a delta function at t=0. Therefore, there must be some other limiting characteristic in the reaction which governs the total rate. A Lindemann kinetic model suggests that this limiting characteristic could be the diffusion rate of Hydrogen radicals in solution. Under this model, the total reaction and rates are given as follows, where B represents the number of Benzene molecules, H dot is the number of Hydrogen radicals, and H₂ is the number of Hydrogen molecules;



Eq 8. As shown in previous work, the photolysis mechanism for Benzene is non-adiabatic and occurs from the quick exchange between electronic and thermal energy via a conical intersection^[4]. The calculated value of J suggests that the homolysis of C-H bonds is extremely quick, and the high instability of phenyl and Hydrogen radicals in close proximity is sufficient to assume that the reverse reaction rate, J₋₁, is also very fast- probably plus or minus an order of magnitude, though this is not confirmed. The formation of diatomic Hydrogen from the encounter pairs (Hydrogen radicals) then is clearly a diffusion limited process, and is likely slow in comparison with the formation and deactivation of radicals- that is, the production rate of Hydrogen gas is dominated by the diffusion rate k. If a first order rate constant is taken as the sum of individual rates, then the following can be shown;

$$r = \sum_i r_i$$

$$\frac{1}{k} \gg \left\{ \frac{1}{J}, \frac{1}{J_{-1}} \right\}$$

∴

$$r \approx k$$

Eq 9. Interpreting the consequence of this leads to an interesting result- that is, that the concentration of Hydrogen radicals (encounter pairs) in solution is approximately constant over time. Starting theoretically, convince yourself that at any point in time, the concentration of encounter pairs in solution should be small. Energetically, a potential well exists for radical deactivation by reforming C-H bonds or by forming Hydrogen gas, so the existence of a high concentration of encounter pairs is not favorable. Alternatively, as the concentration of Hydrogen radicals increases, so must the concentration of Benzene radicals which in turn increases the probability for radical deactivation. Either way, it does not take much reasoning to conclude that the number of Hydrogen radicals in solution should not be increasing massively over time- it simply is too unstable of a system. Also, a very crucial assumption is made here, and the following logic is only valid if this condition is adhered to; that there is a largely excess amount of Benzene present at any time t. From Eq 7 it is clear that from the absorption of a photon produces Hydrogen radicals at rate J, and that these radicals are deactivated at rate J₋₁. Therefore;

$$-\frac{dB(t)}{dt} = \frac{dH \cdot (t)}{dt} = (J - J_{-1})B$$

Eq 10. If the initial concentration of Benzene is massive enough such that the concentrations before and after irradiation are approximately equal, then the following can be said;

$$0 \approx \frac{dH \cdot (t)}{dt} \approx (J - J_{-1})B$$

Eq 11. Which implies that for very large concentrations of Benzene, the change in production and deactivation rate of encounter pair radicals from a change in Benzene concentration is negligible (keeping in mind that at small Benzene concentrations, this approximation no longer works). Referencing Eq 8, both the production and deactivation rates were taken to be approximately zero considering the very long diffusion time for encounter pairs (that is, the total rate of Hydrogen gas production is dominated by the diffusion rate) which accounts for how the J-J₋₁ term in Eq 10 can remain valid for some initial concentration of Benzene B>0. Solving the remaining ODE, it is seen that the number of encounter pair radicals at time t is approximately constant. This will result in a very useful simplification in a few steps;

$$H \cdot (t) \approx C$$

$$C \in R$$

Eq 12. However, without any other considerations, this model suggests that the concentration of Hydrogen gas over time should be linear. That is;

$$\frac{dH_2(t)}{dt} = kH \cdot (t) = kC$$

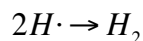
$$H_2(t) = kCt + c$$

Eq 13. Clearly, this too is not supported empirically, but at small time intervals ($0 < t \ll 700$ sec), a linear model actually does nicely represent the data. The issue is that the linear model begins to fall apart as $t \rightarrow \infty$ because $H_2(t) = kCt + c$ is not bounded. A linear model with an attenuation factor which forces the solution to have a steady state would be much more realistic. In practice, many if not all chemical systems have an equilibrium constant k_{eq} which can be defined in a number of ways- however, the important take-away is the second line;

$$k_{eq} \propto \frac{y_i}{x_i} \propto \frac{q_i}{p_i} \propto \frac{[H_2]}{V}$$

$$k_{eq} \in R$$

Eq 14. The consequence of these assumptions is that a steady state is reached at some critical concentration of Hydrogen gas. This fact can be used to help introduce the attenuation character into the linear model described above. Rationally, it can be assumed that the rate of Hydrogen gas production should be proportional to the concentration of H_2 in the chamber. That is, the rate will be high for low concentrations and it approaches zero as the concentration converges to the steady state S . Recall that a rate for a simple unidirectional reaction can be given as K . Keep in mind that this rate constant does not take into account diffusion, and is only used for the following illustration. Formally;



$$K = \frac{[H \cdot]^2}{[H_2]}$$

\therefore

$$\lim_{[H_2] \rightarrow 0} K = \lim_{[H_2] \rightarrow 0} \frac{[H \cdot]^2}{[H_2]} = \infty$$

$$\lim_{[H_2] \rightarrow \infty} K = \lim_{[H_2] \rightarrow \infty} \frac{[H \cdot]^2}{[H_2]} = 0$$

Eq 15. Even though K is not accurate for this system, the illustration of what happens as the concentration of Hydrogen gas increases should also be true for a diffusion limited model. Therefore, the general form of an ODE which models the concentration of Hydrogen gas over time and has a steady state at $\epsilon = \alpha/H_2(t)$ can be given as;

$$\frac{dH_2(t)}{dt} = \alpha - \epsilon H_2(t) : \{\alpha, \epsilon\} \in R$$

Eq 16. All that remains then is to determine the values of α & ϵ . It was assumed in Eq 11 that α corresponds to some diffusivity coefficient of Hydrogen radicals in solution. Collision theory gives a simple way to calculate Z, the collision frequency- this can then be related to some rate k. For reactants A & B, the following can be said;

$$Z = n_A n_B \sigma_{AB} \sqrt{\frac{8k_b T}{\pi \mu_{AB}}}$$

Eq 17. Where n_i is the number density of reactant i, σ_{AB} is the reaction cross section, k_b is Boltzmann's constant, T is temperature, and μ_{AB} is the reduced mass of the reactants. Z is therefore given in units of collisions $m^{-3} sec^{-1}$. To convert this frequency to a rate, two pieces of information are needed. Firstly, the volume of the chamber V, and the quantum yield of a collision of encounter pairs, ϕ . Then;

$$k = ZV\phi = n_A n_B \sigma_{AB} \phi V \sqrt{\frac{8k_b T}{\pi \mu_{AB}}}$$

Eq 18. Knowing that in this reaction reactants A and B both correspond to Hydrogen radicals, and expressing number density as the quotient of number of molecules, N, and volume, one obtains;

$$k = \left(\frac{N^2}{V^2}\right) \sigma_H \phi V \sqrt{\frac{8k_b T}{\pi \mu_H}} = \frac{N^2 \sigma_H \phi}{V} \sqrt{\frac{8k_b T}{\pi \mu_H}}$$

Eq 19. And the constants are given as follows, where r_H and m_H are the Bohr radius and mass of a Hydrogen atom respectively.

$$\sigma_H = \pi(2r_H)^2$$

$$\mu_H = \frac{m_H^2}{2m_H}$$

$$\phi = 1$$

Eq 20. Letting $k=\alpha$ from Eq 15, the following rate law is deduced;

$$\frac{dH_2(t)}{dt} = \frac{N^2 \sigma_H \phi}{V} \sqrt{\frac{8k_b T}{\pi \mu_H}} - \varepsilon H_2(t)$$

Eq 21. From Eq 11 it was assumed that the number of Hydrogen radicals at any time was equal to a constant. In Eq 16, the number density of these encounter pairs was called and eventually expressed as the quantity N^2 . Formally, it is given as;

$$N^2 = (J - J_{-1})^2 B^2 = \gamma$$

Eq 22. The value γ is introduced for simplicity, and also so it is clear that N^2 is a parameter value. While the forward reaction rate J was calculated in Eq 1, the inverse rate J_{-1} is not known. We assumed that B remains approximately constant throughout the course of the reaction because it exists in large quantities. Therefore, J_{-1} will be found from curve fitting with empirical data such that;

$$\frac{dH_2(t)}{dt} = \frac{\gamma \sigma_H \phi}{V} \sqrt{\frac{8k_b T}{\pi \mu_H}} - \varepsilon H_2(t)$$

$$\gamma \in R$$

Eq 23. Therefore, it can be seen that a steady state for the system exists when;

$$\frac{dH_2(t)}{dt} = 0$$

$$\varepsilon H_2^* = \frac{\gamma \sigma_H \phi}{V} \sqrt{\frac{8k_b T}{\pi \mu_H}}$$

$$\varepsilon = \frac{\gamma \sigma_H \phi}{H_2^* V} \sqrt{\frac{8k_b T}{\pi \mu_H}}$$

Eq 24. Where H_2^* corresponds to an equilibrium concentration of Hydrogen gas. Empirically, this value has been determined to be ≈ 250 ppm. Plugging in and simplifying;

$$\frac{dH_2(t)}{dt} = \frac{\gamma \sigma_H \phi}{V} \sqrt{\frac{8k_b T}{\pi \mu}} \left(1 - \frac{H_2(t)}{H_2^*} \right)$$

Eq 25. Then separating variables and integrating;

$$\int \frac{dH_2(t)}{\left(1 - \frac{H_2(t)}{H_2^*}\right)} = \int \frac{\gamma\sigma_H\phi}{V} \sqrt{\frac{8k_bT}{\pi\mu}} dt$$

$$-H_2^* \ln \left| 1 - \frac{H_2(t)}{H_2^*} \right| = \frac{\gamma\sigma_H\phi}{V} \sqrt{\frac{8k_bT}{\pi\mu}} t + c$$

$$H_2(t) = H_2^* \left(1 - \exp \left[\frac{-\gamma\sigma_H\phi}{H_2^*V} \sqrt{\frac{8k_bT}{\pi\mu}} t - \frac{c}{H_2^*} \right] \right)$$

Eq 26. And solving for c with the given initial condition;

$$H_2(0) = 25$$

$$25 = H_2^* \left(1 - \exp \left[-\frac{c}{H_2^*} \right] \right)$$

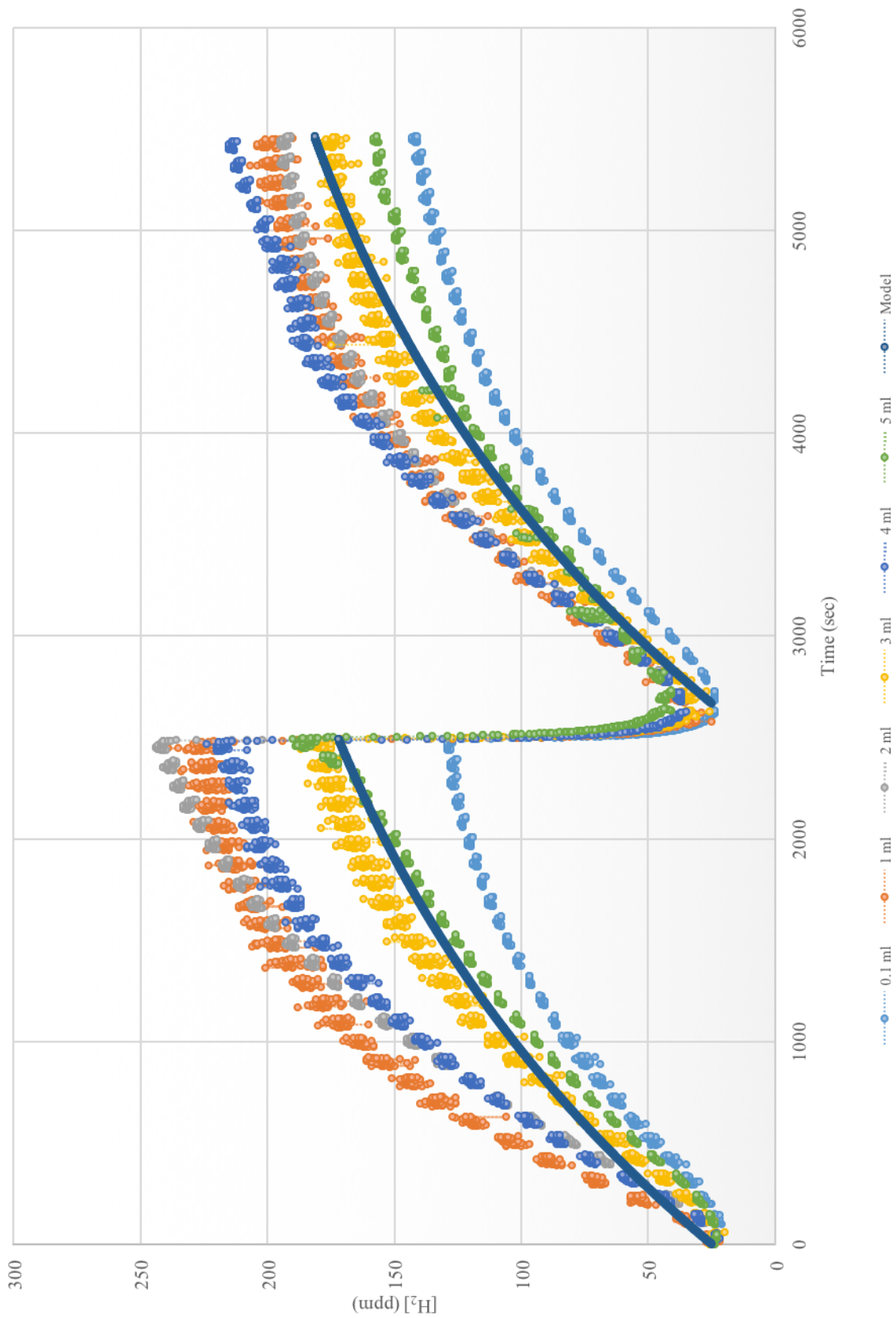
$$c = -H_2^* \ln \left| 1 - \frac{25}{H_2^*} \right|$$

Eq 27. Therefore;

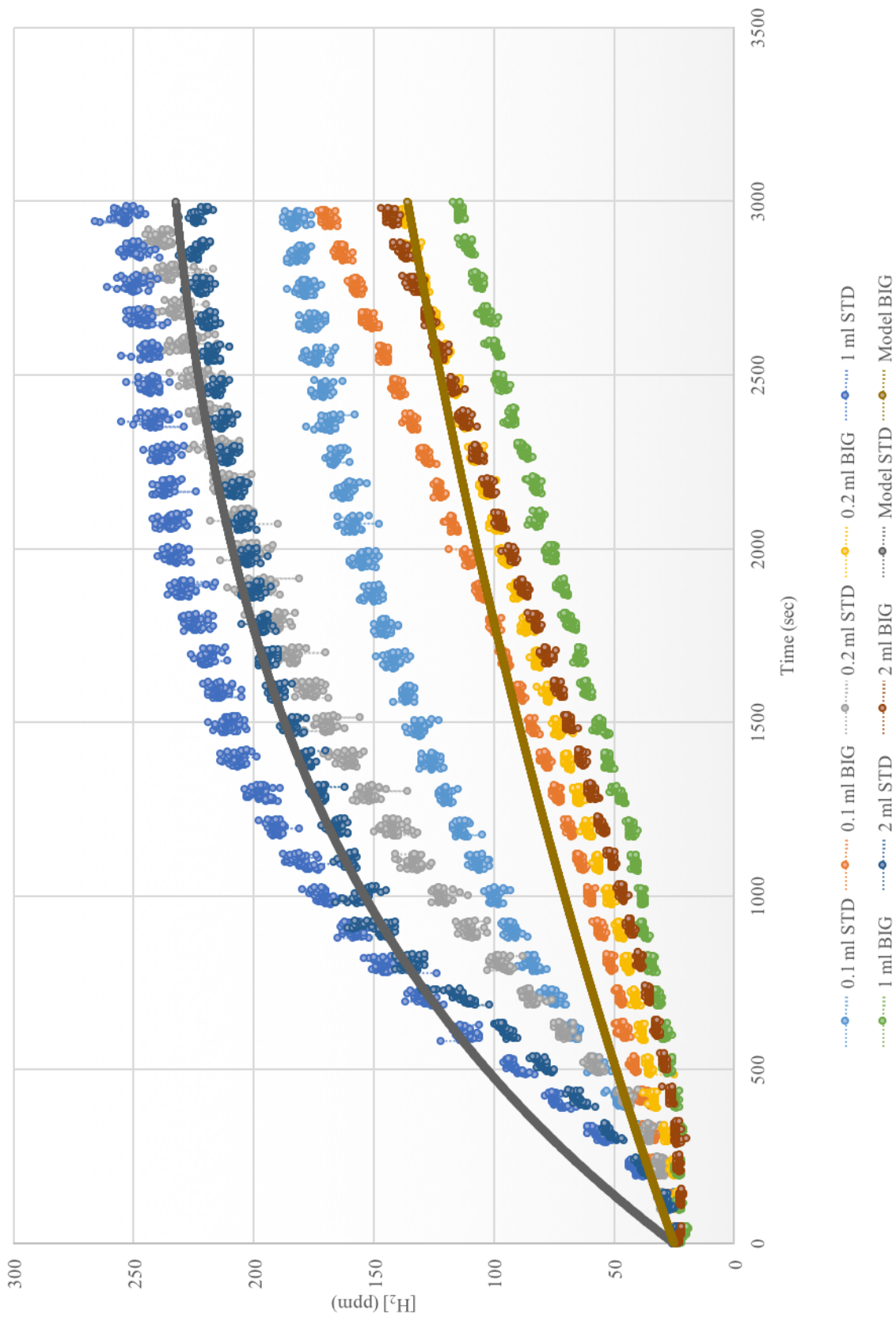
$$H_2(t) = H_2^* \left(1 - \exp \left[\frac{-\gamma\sigma_H\phi}{H_2^*V} \sqrt{\frac{8k_bT}{\pi\mu}} t + \ln \left| 1 - \frac{25}{H_2^*} \right| \right] \right)$$

To assist in developing this model, empirical data was collected and was compared with the predictions of the model. Figure 1 shows a series of curves measuring the concentration of H₂ over time at what is referred to as STD volume ($\approx 0.00068 \text{ m}^3$). The model from equation 27 is overlaid on this data with a γ value of 10^{13} . Figure 2 shows a series of curves also measuring the concentration of H₂ over time, but at two different volumes to validate the assumption that evolution rate is inversely proportional to volume. The STD volume is the same value as in figure 1, and the BIG volume is ($\approx (0.00068 + 0.00123) \text{ m}^3$). The γ values for both curves in this model is $2 \cdot 10^{13}$.

[H₂] vs. Time, 173 nm, Constant Volume (Fig. 1)



[H₂] vs. Time, 173 nm, Varying Volume (Fig. 2)



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