**Supplementary Materials for:**

# Formulation of Reaction Kinetics for Cyclohexanone Ammoximation Catalyzed by a Clay-based Titanium Silicalite-1 Composite in a Semi-Batch Process

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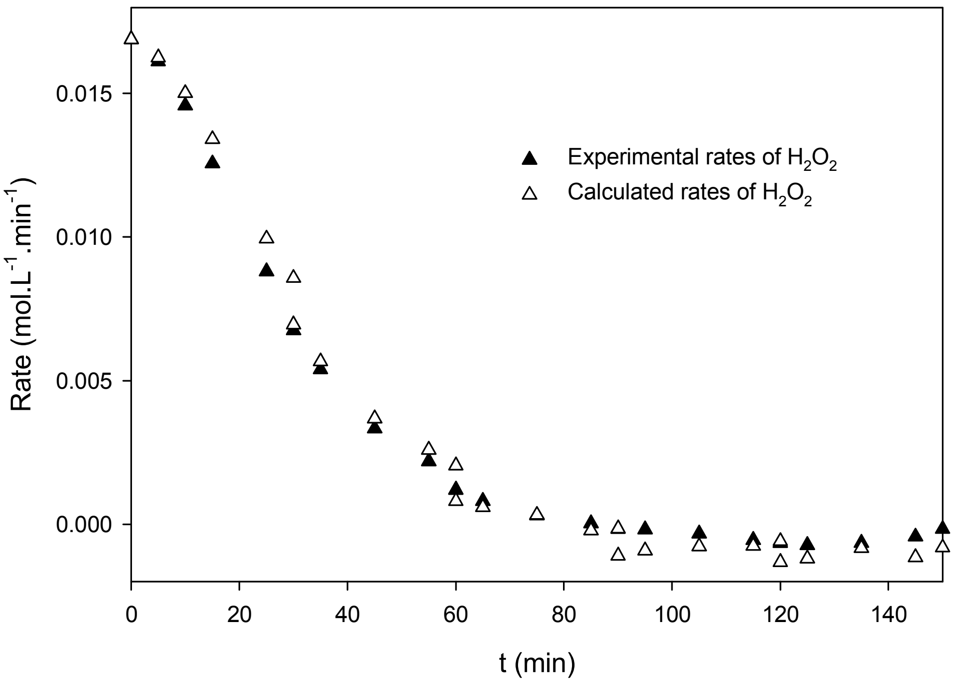


**Figure S1.** Curve fitting for power law model at 80 °C ($H_2O_2$).

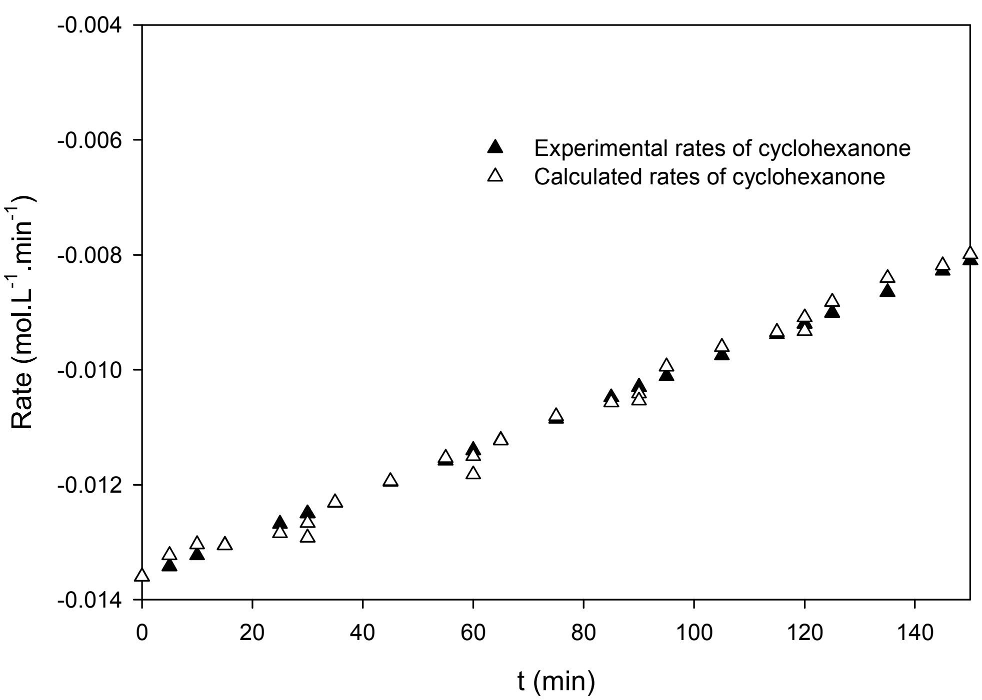


**Figure S2.** Curve fitting for power law model at 80 °C (Cyclohexanone).

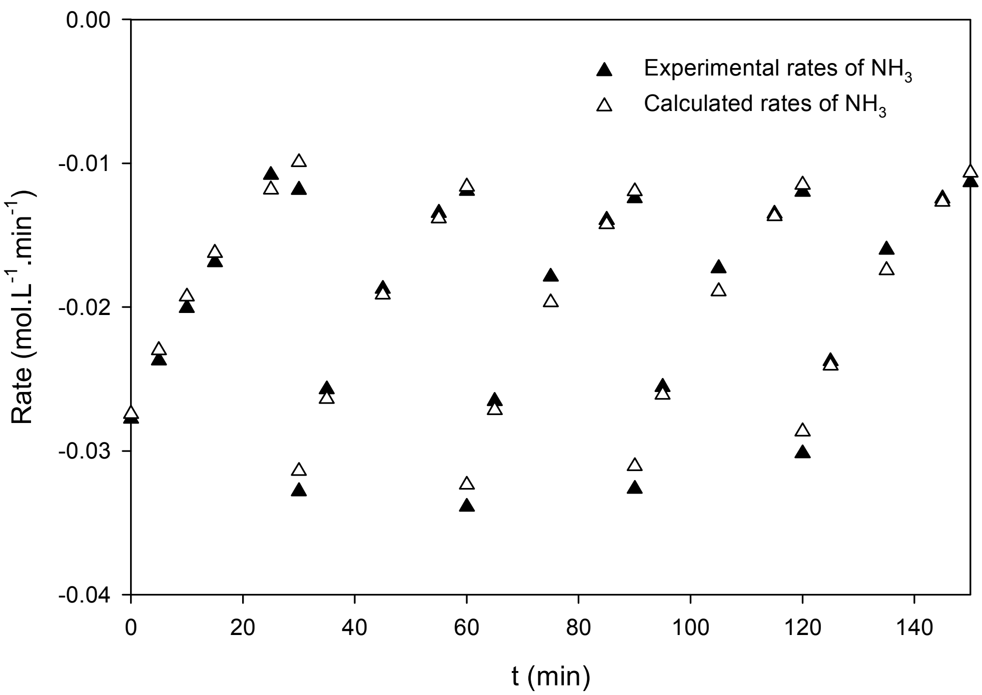


**Figure S3.** Curve fitting for power law model at 80 $^{o}$C ($NH_3$).

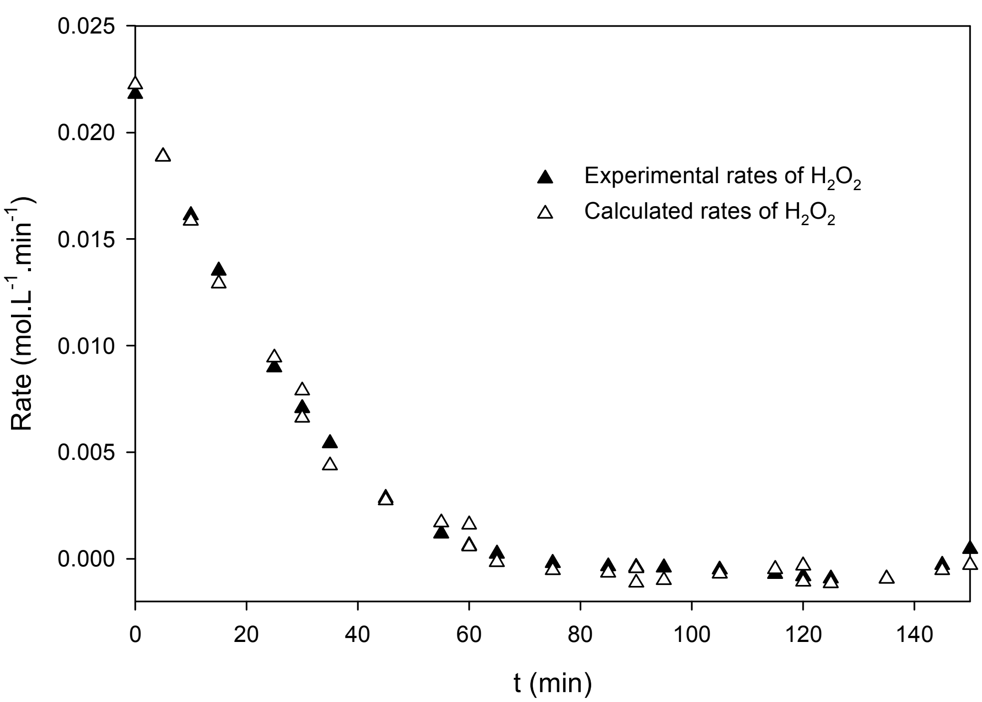


**Figure S4.** Curve fitting for power law model at 70 $^{o}$C ($H_2O_2$).

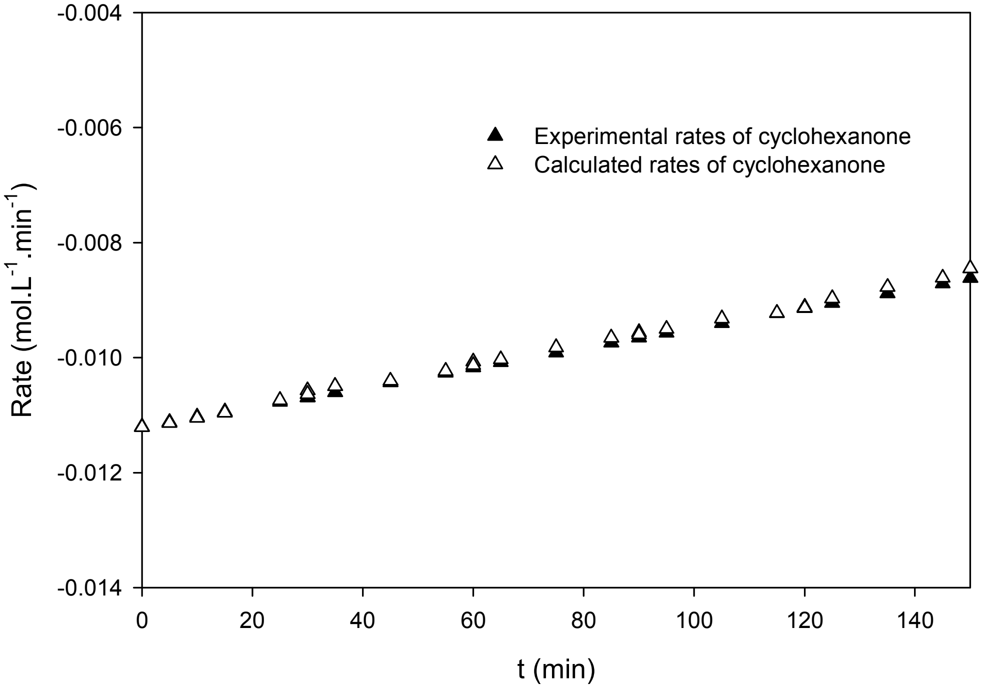


**Figure S5.** Curve fitting for power law model at 70 $^oC$ (Cyclohexanone).

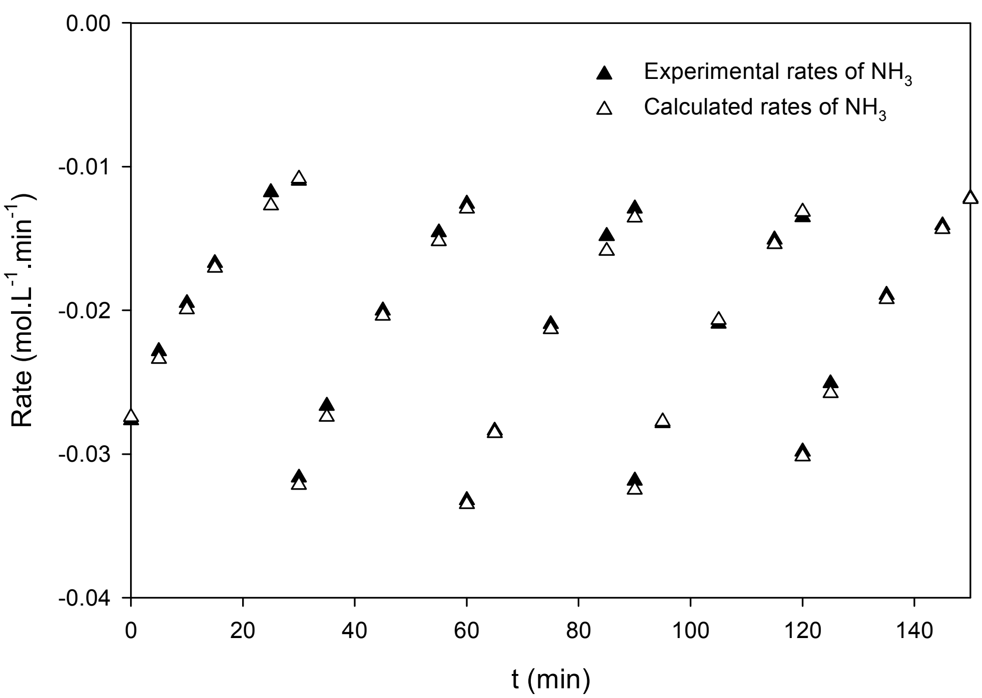


**Figure S6.** Curve fitting for power law model at 70 $^oC$ ($NH_3$).

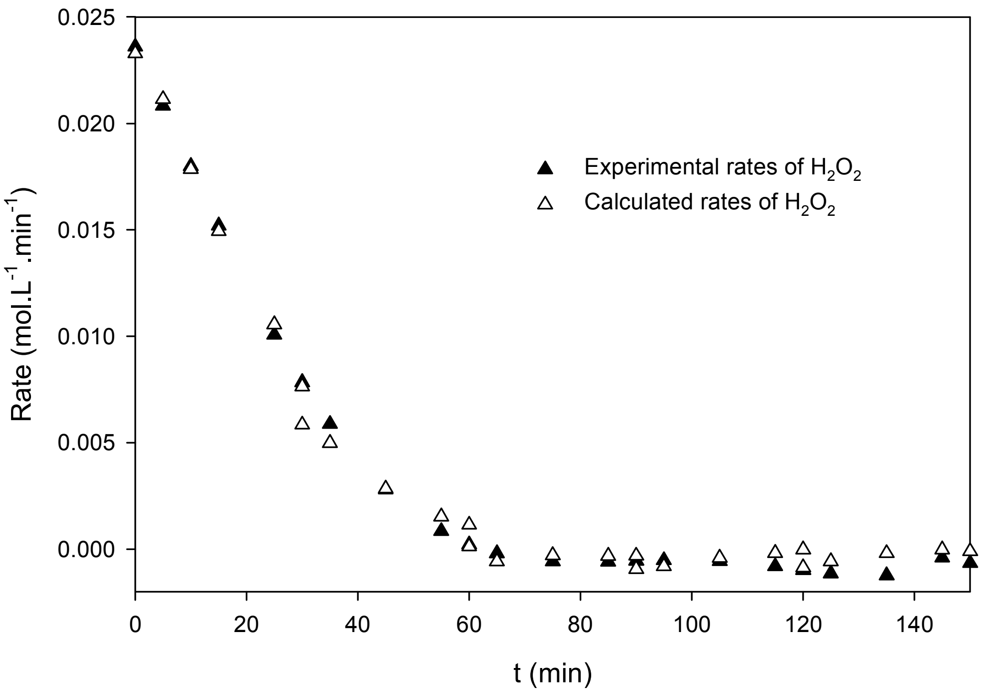


**Figure S7.** Curve fitting for power law model at 60 $^{o}$C ($H_2O_2$).

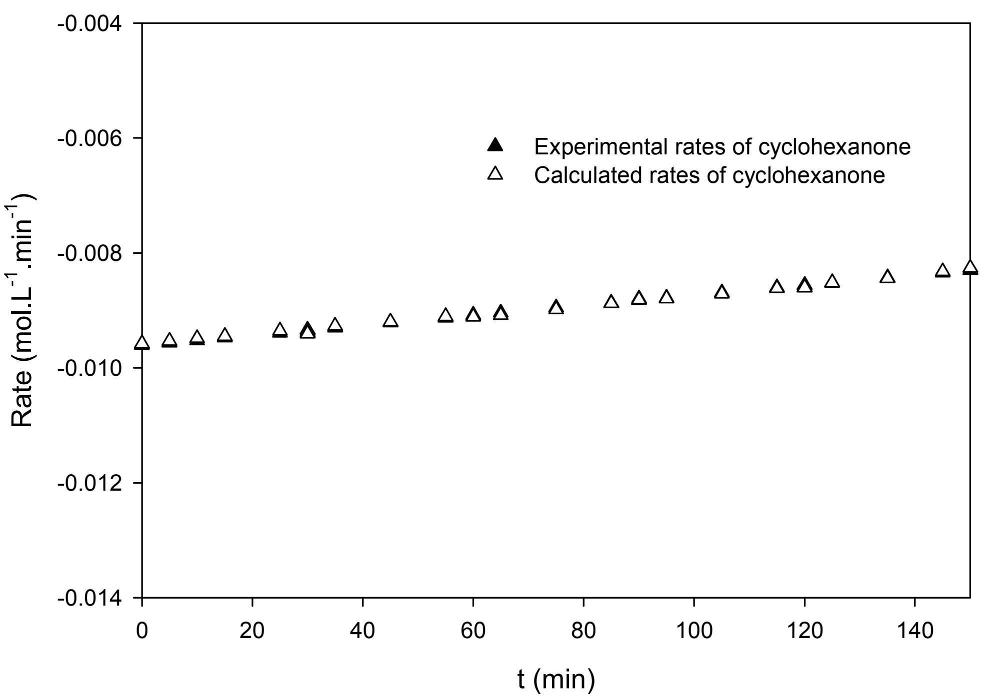


**Figure S8.** Curve fitting for power law model at 60 $^{o}$C (Cyclohexanone).

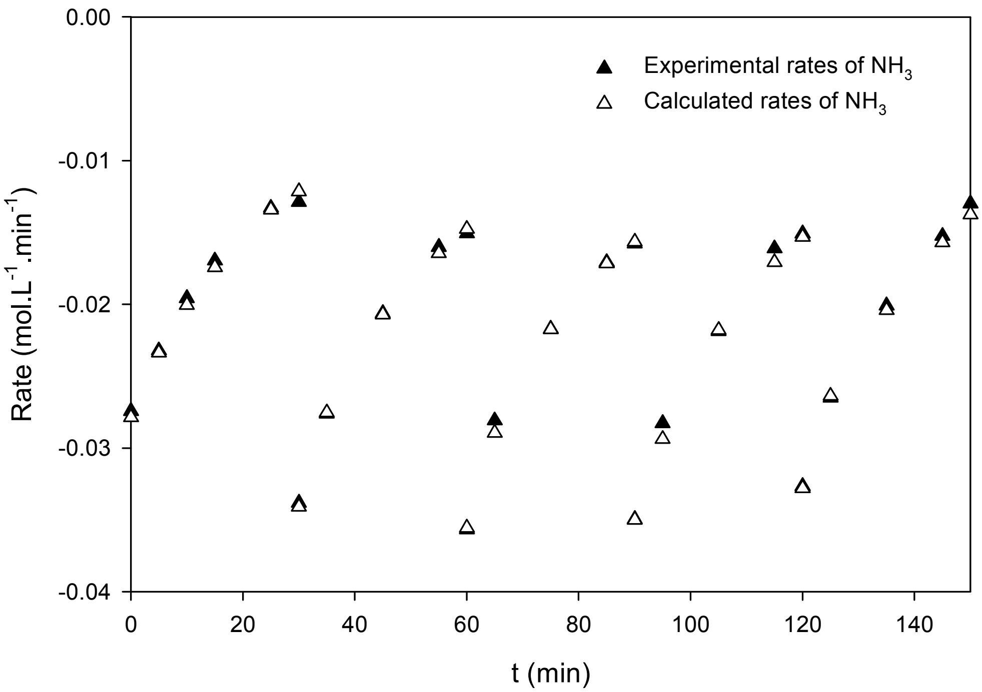


**Figure S9.** Curve fitting for power law model at 60 °C ($NH_3$).

**Deviation of rate law**

Following is the development of the rate law that describes the intrinsic kinetic based on the L-H mechanism:

Define site [A] = $\theta_1$ and site [B] = $\theta_2$. The site with adsorbed molecule is presented in the form of $\theta_{\text{site, adsorbed molecule}}$. For example, the Ti active site with adsorbed $H_2O_2$ is presented as $\theta_{1,\,H_2O_2}$ and the vacant Ti active site is presented as $\theta_{1V}$ etc.

The rate law of the RDS, Eq. (10), can be written as,

$$R = k_4^{'}\theta_{1,H_2O_2}\theta_{1,NH_3}\theta_{2,Cyclo} \tag{S1}$$

The rate equation of $H_2O_2$ adsorption is,

$$r_1 = k_1\theta_{1V}C_{H_2O_2} - k_{-1}\theta_{1,H_2O_2}$$

$$r_1 = k_1\left[\theta_{1V}C_{H_2O_2} - \frac{\theta_{1,H_2O_2}}{K_1}\right] \qquad \text{where } K_1=\frac{k_1}{k_{-1}}$$

Considering surface reaction is rate controlling, therefore

$$k_4^{'} << k_1,\ k_2,\ k_3$$

i.e. $\frac{r_1}{k_1} \approx 0 \approx \frac{r_2}{k_2} \approx \frac{r_3}{k_3}$

Hence, $\theta_{1,H_2O_2} = K_1\theta_{1V}C_{H_2O_2}$ (S2)

Similarly, the rate equation of $NH_3$ and cyclohexanone adsorption steps give,

$$\theta_{1,NH_3} = K_2\theta_{1V}C_{NH_3} \text{ and} \tag{S3}$$

$$\theta_{2,Cyclo} = K_3\theta_{2V}C_{Cyclo} \tag{S4}$$

Site balance for [A] gives,

$$1 = \theta_{1V} + \theta_{1,H_2O_2} + \theta_{1,NH_3} \tag{S5}$$

Substitute Eqs. (20) and (21) into Eq. (23) becomes,

$$\theta_{1V} = \frac{1}{1 + K_1C_{H_2O_2} + K_2C_{NH_3}} \tag{S6}$$

Site balance for [B] gives,

$$1 = \theta_{2V} + \theta_{2,Cyclo} \tag{S7}$$

Substitute Eq. (22) into Eq. (25) gives,

$$\theta_{2V} = \frac{1}{1 + K_3C_{Cyclo}} \tag{S8}$$

Finally, by substituting Eqs. (S2), (S3), (S4), (S6) and (S8) into Eq. (S1), which is the RDS of the proposed mechanism, leads to the rate law that describes the intrinsic kinetic based on the L-H model:

$$R = \frac{k_4^{'}K_1K_2K_3 \cdot C_{H_2O_2}C_{NH_3}C_{Cyclo}}{\left(1 + K_1C_{H_2O_2} + K_2C_{NH_3}\right)^2 \cdot \left(1 + K_3C_{Cyclo}\right)} \tag{S9}$$

Similarly, the corresponding rate models derived from the E-R-1 and E-R-2 proposals are presented in Eqs. (S10) and (S11):

$$R = \frac{k_6^{'} K_1 C_{H_2O_2} C_{NH_3} C_{Cyclo}}{\left(1 + K_1 C_{H_2O_2}\right)} \tag{S10}$$

$$R = \frac{k_9^{'} K_1 K_3 C_{H_2O_2} C_{Cyclo} C_{NH_3}}{\left(1 + K_1 C_{H_2O_2}\right)\left(1 + K_3 C_{Cyclo}\right)} \tag{S11}$$

**Plotting ln k versus 1/T,**

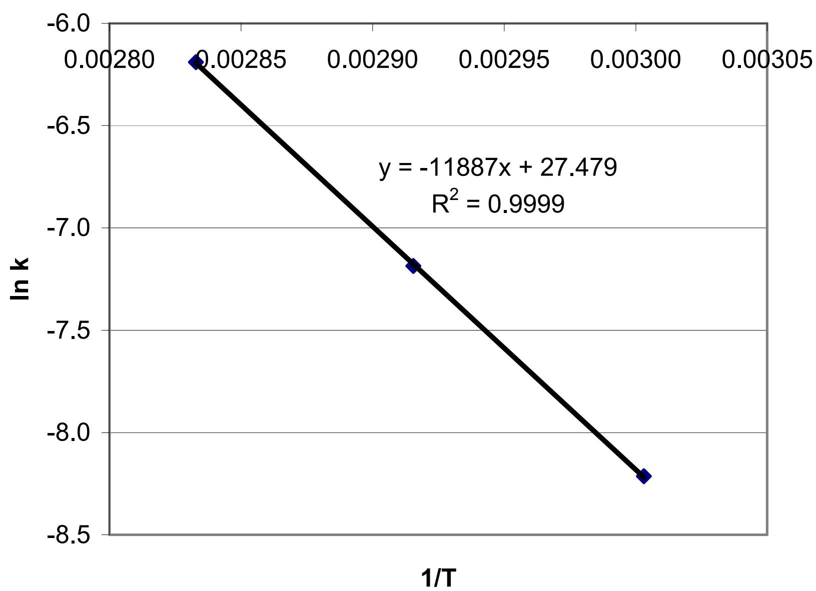


**Figure S10.** ln k vs 1/T plot for determination of activation energy and preexponential factor.

$$E_a = (11887 \times 8.314)\ \text{J/mol}$$
$$= 9.883 \times 10^4\ \text{J/mol}$$

and $k_o = e^{27.479} = 8.590 \times 10^{11}$ (with the same unit as k)