A Pseudo-Order Kinetic Analysis

The file "Pseudo-Order Data" contains kinetic data for the reaction:

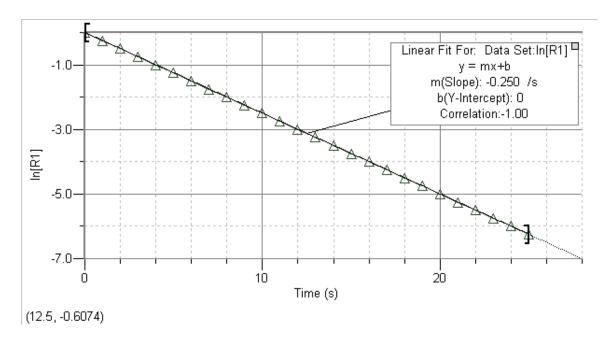
$$R_1 + R_2 + R_3 \rightarrow Products$$

Each page contains data for a pseudo-order experiment in which the concentration of one reactant is significantly smaller than the concentration of the other two reactants. Using this data determine the reaction order for each reactant, the three observed pseudo-order rate constants, the reaction's true rate constant and the overall rate law.

The rate law for this reaction is of the general form

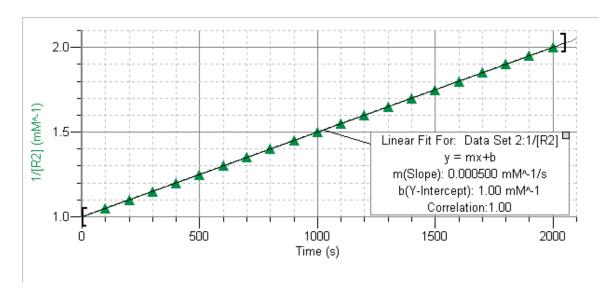
rate =
$$k[R_1]^{\alpha}[R_2]^{\beta}[R_3]^{\gamma}$$

The data on Page 1 show first-order kinetics because a plot of $ln[R_1]$ vs. time is linear, as shown here:



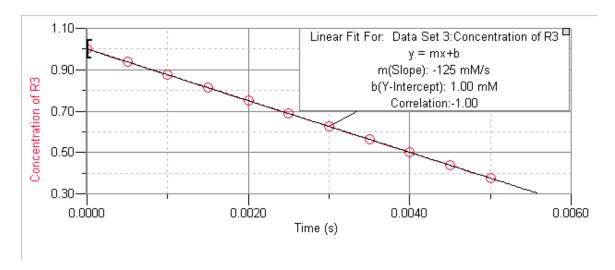
The reaction order for R_1 (α) is 1 and the observed rate constant, $(k_{\rm obs})_1$, which is equivalent to $k[R_2]^{\beta}[R_3]^{\gamma}$ is $0.250~{\rm s}^{-1}$.

The data on Page 2 show second-order kinetics because a plot of $1/[R_2]$ vs. time is linear, as shown here:



The reaction order for R_2 (β) is 2 and the observed rate constant, $(k_{\rm obs})_2$, which is equivalent to $k[R_1][R_3]^{\gamma}$ is $5.00\times10^{-4}~{\rm mM}^{-1}~{\rm s}^{-1}$ (note that α for R_1 is 1 as determined above).

The data on Page 3 show zero-order kinetics because a plot of $[R_3]$ vs. time is linear, as shown here:



The reaction order for R_3 (γ) is 0 and the observed rate constant, $(k_{obs})_3$, which is equivalent to $k[R_1][R_2]^2$ is 125 mM/s.

The rate law for the reaction, therefore, is

$$rate = k[R_1][R_2]^2$$

To find the rate constant, k, we can use any of the known observed rate constants; thus $(k_{\rm obs})_1 = k[{\rm R}_2]^{\beta} [{\rm R}_3]^{\gamma} = k[{\rm R}_2]^2 = k(500 \ {\rm mM})^2 = 0.250 \ {\rm s}^{-1}$

which gives k as 1.0×10^{-6} mM⁻² s⁻¹. Or, using $(k_{obs})_2$

$$(k_{\text{obs}})_2 = k[R_1]^{\alpha}[R_3]^{\gamma} = k[R_1] = k(500 \text{ mM}) = 5.00 \times 10^{-4} \text{ mM}^{-1} \text{ s}^{-1}$$

which gives k as 1.0×10^{-6} mM⁻² s⁻¹. Or, using $(k_{obs})_3$

$$(k_{\text{obs}})_3 = k[R_1]^{\alpha}[R_2]^{\beta} = k[R_1][R_2]^2 = k(500 \text{ mM})(500 \text{ mM})^2 = 125 \text{ mM/s}$$

which gives k as 1.0×10^{-6} mM⁻² s⁻¹.