Finding a Rate Law Using the Method of Initial Rates

Consider the reaction between hydrogen peroxide, H_2O_2, and iodide, I^-, to form triodide, I_3^-

$$H_2O_2(aq) + 3I^-(aq) + 2H^+(aq) \rightarrow I_3^-(aq) + 2H_2O$$

The initial rate of the reaction is measured by adding a very small amount of thiosulfate, $S_2O_3^{2-}$, and a solution of starch. Because thiosulfate reacts quickly with triodide as it forms, I_3^- immediately converts back to I^-. Once all of the thiosulfate is used up, the formation of I_3^- becomes permanent and, because it forms a strong blue-colored complex with starch, the solution turns dark blue. A buffer is included in the reaction to maintain the pH so that we do not need to consider the effect of H^+ on the reaction's rate law. The differential rate law for this reaction is

$$R = -\frac{\Delta[S_2O_3^{2-}]}{\Delta t} = k[I^-]^{\alpha}[H_2O_2]^{\beta}[S_2O_3^{2-}]^{\gamma}$$

where R is the initial rate and $\alpha, \beta,$ and γ are reaction orders. The following grid shows the set of experiments we will run. We will use the first four experiments to determine the rate law and then use the last experiment to test our result.

run	$[I^-]$ (M)	$[H_2O_2]$ (M)	$S_2O_3^{2-}$ (M)	time (s)	rate (M/s)	rate constant
1	0.020	0.020	5.0×10^{-4}	68.86	7.26×10^{-6}	0.0182
2	0.020	0.040	5.0×10^{-4}	31.17	1.60×10^{-5}	0.0200
3	0.020	0.020	1.0×10^{-3}	132.14	7.57×10^{-6}	0.0190
4	0.040	0.020	5.0×10^{-4}	35.06	1.43×10^{-5}	0.0178
5	0.040	0.040	1.0×10^{-3}	33	3.01×10^{-5}	0.0188

The times recorded here were the average of four independent measurements. The rates for Run 1 and Run 2 give α as 1; the rates for Run 1 and Run 3 give β as 0; the rates for Run 1 and Run 4 give γ as 1. Collectively, these show that the rate law is

$$R = -\frac{\Delta[S_2O_3^{2-}]}{\Delta t} = k[I^-][H_2O_2]$$

The rate constant for each of the first four runs was calculated using this rate law and the concentrations of iodide and peroxide used in that run with units of $M^{-1}\ s^{-1}$. The rate constant listed for Run 5 is the average of the rate constants for Runs 1–4. The predictated rate and time for Run 5 is based on the final rate law and the average rate constant. The experimental result for Run 5 was about 16 seconds.