

# The Effect of Ionic Strength on Reaction Rate

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## Abstract

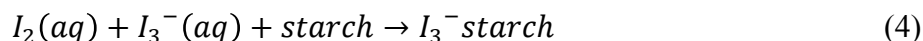
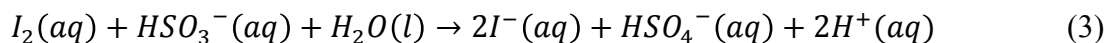
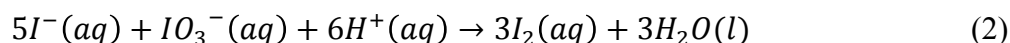
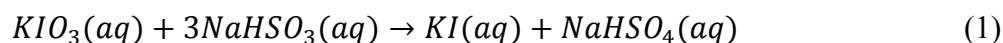
The rate of the reaction between potassium iodate and sodium bisulfite was determined for reactions with different concentrations of spectator ions. The goal of this experiment was to determine the relationship between ionic strength and reaction rate. For this reaction, the experimentally determined rate constant, at zero ionic strength ( $k_0$ ) was  $0.56 \pm 0.04 M^{-1} s^{-1}$  and the charge of the transition state complex ( $z_1 z_2$ ) was determined to be  $-0.44 \pm 0.05$ . The negative value of  $z_1 z_2$  indicates that the charges of the ions making up the transition state complex have opposite signs.<sup>2</sup> As a result; the transition state complex is less stabilized by ions in solution, than the individual reactants. This causes the reaction rate to decrease.

## Introduction

The rate of a reaction is a measure of how quickly reactants are consumed to form products.<sup>1</sup> The reaction rate is dependent upon the concentration of species involved in the rate determining step, as well as the ionic strength (I) of the reaction.<sup>1</sup> Depending on the reaction mechanism, increasing the ionic strength may accelerate or slow the reaction.<sup>2</sup> If the transition state of the reaction is a complex formed by two cations or two anions, then the reaction rate increases with increasing ionic strength.<sup>2</sup> This is because the magnitude of the charge of the transition state complex is higher than that of each individual reactant; thus, the transition state can be stabilized by ions in solution more than the separate reactants.<sup>2</sup> If the transition state complex is formed by an anion and a cation, the reaction rate decreases with increasing ionic

strength.<sup>1</sup> This is due to the preferred stabilization of the reactants rather than the transition state complex which has a smaller total charge than each reactant.<sup>2</sup> The effect of ionic strength on reaction rate is referred to as the kinetic salt effect.<sup>1</sup>

The purpose of this experiment was to observe the effect of ionic strength on reaction rate for the reaction of sodium bisulfite and potassium iodate. The observed reaction scheme is shown below in Equations one through four. The first step of this reaction, shown in Equation 1, is rate limiting and determines the overall reaction rate.<sup>1</sup> If the transition state of this reaction is a complex of two charges with opposite signs, a decrease in reaction rate should be observed as ionic strength is increased.<sup>2</sup> Conversely, if the transition state complex contains two like charges, the reaction rate will increase with increasing ionic strength.<sup>2</sup>



## Experimental

The procedure for this experiment was procured from Huffman, C. *Reaction Rate vs. Ionic Strength*, Western Carolina University 2015. All chemicals were purchased from Sigma-Aldrich Chemical Company.

Aqueous stock solutions of potassium iodate, sodium bisulfite, and magnesium sulfate were prepared according to the measurements found in the table 1, below. Note the use of  $Na_2S_2O_5$  to make the  $NaHSO_3$  solution.

### Table 1: Solution preparation for reaction stock solutions.

	<b>KIO<sub>3</sub></b>		<b>NaHSO<sub>3</sub></b>		<b>1 M MgSO<sub>4</sub></b>
m(KIO <sub>3</sub> ) (g)	21.4047±0.0005	m(Na <sub>2</sub> S <sub>2</sub> O <sub>5</sub> ) (g)	0.4750±0.0005	m(MgSO <sub>4</sub> ·7H <sub>2</sub> O) (g)	61.6405±0.0005
V (mL)	1000.00±0.30	V (mL)	500.00±0.20	V (mL)	250.00±0.12
conc (M)	0.100024	conc (M)	0.0100	conc (M)	1.0004

Magnesium sulfate solutions, with concentrations of 0.50018M, 0.20007M, 0.10004M, .05002M, and 0.01000M, were prepared via serial dilutions. The starch solution was prepared by dissolving starch in boiling water. The heat activates the starch, allowing it to act as a reaction indicator. The cooled solution was diluted to the desired 1% concentration by adding 100mL of water per gram of starch.

The amount of potassium iodate and sodium bisulfite used for each reaction remained constant, and ionic strength was varied by adding different amounts of magnesium sulfate salt. Sodium bisulfite was the limiting reactant. Below, table 2 displays the amount of starch, the amount of magnesium sulfate, and the ionic strength of each reaction. For each measurement, 3 mL sodium bisulfite stock solution, and the appropriate amounts of magnesium sulfate and starch were added to a small beaker. Then, 6 mL potassium iodate stock solution was introduced into the beaker using a graduated cylinder. Immediately after adding the potassium iodate, a timer was started and the reaction mixture was swirled briefly. The timer was stopped as soon as the reaction mixture started to turn blue. This color change, caused by the starch indicator, indicates the completion of the reaction. Three trials were performed for each reaction.

**Table 2: Amounts of MgSO<sub>4</sub> and starch for each reaction.**

Rxn #	Concentration			Ionic Strength (M)
	MgSO <sub>4</sub> (M)	V <sub>MgSO<sub>4</sub></sub> (mL)	V <sub>starch</sub> (mL)	
1	0	0	6	0.042008
2	1	2	4	0.57553
3	1	4	2	1.1090
4	0.5	2	4	0.30877
5	0.2	4	2	0.25542
6	0.1	4	2	0.14871
7	0.1	2	4	0.095360
8	0.05	2	4	0.068684
9	0.01	2	4	0.047344

The measured reaction time and the concentrations of reactants were used to determine the rate constant (k) of each reaction. Equation 5 and equation 6 can be related to yield the relationship in equation 7 which was used to calculate the rate constant for each reaction.

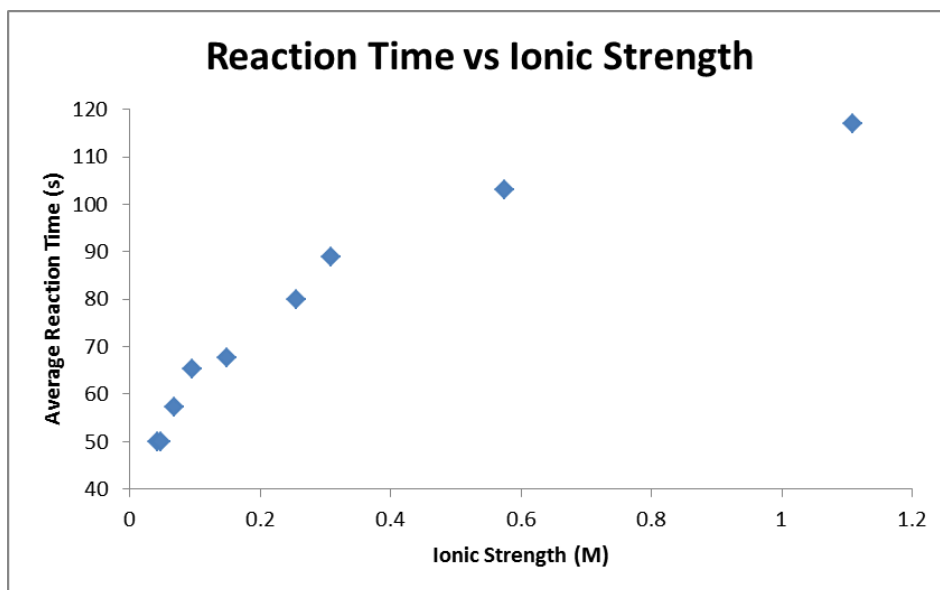
$$\text{Rate} = k[\text{IO}_3^-][\text{HSO}_3^-] \quad (5)$$

$$\text{Rate} = -\frac{\Delta[\text{HSO}_3^-]}{\Delta t} \quad (6)$$

$$k = \frac{1}{t[\text{IO}_3^-]} \quad (7)$$

## Results

The times measured in each trail were averaged together to give the average time for each reaction to go to completion. It was observed that reaction rate did change with ionic strength. Figure 1 shows the relationship between ionic strength and time. As the ionic strength increased, the reaction time also increased.



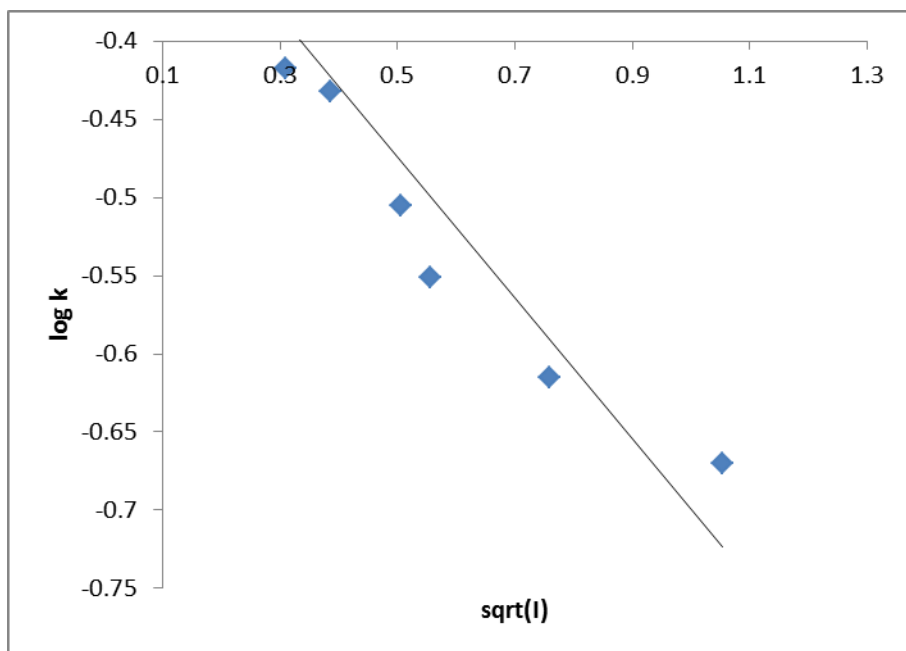
**Figure 1: Reaction time as a function of ionic strength.**

Using equation 3, shown above, the rate constant was determined for each reaction. Table 3 lists the rate constants at a 95% confidence interval, as well as the average times, for reactions varying in ionic strength.

**Table 3: Equilibrium constant and average time for reactions with varying ionic strength.**

Rxn #	Ionic Strength (M)	Average Time (s) (95%,3)	Rate Constant ( $M^{-1}s^{-1}$ ) (95%,3)
1	0.042008	50±9	0.50±0.08
2	0.047344	103±2	0.50±0.02
3	0.068684	117±2	0.436±0.007
4	0.095360	89±3	0.382±0.006
5	0.14871	80.00	0.37±0.02
6	0.25542	68±4	0.31243
7	0.30877	65±1	0.28±0.01
8	0.57553	57±1	0.243±0.004
9	1.10905	50±2	0.214±0.003

The relationship between the rate constant and ionic strength is shown in figure 2 where  $\log k$  is plotted as a function of the square root of ionic strength.



**Figure 2: Relationship between rate constant and ionic strength.** Values are plotted as  $\log k$  vs.  $\sqrt{I}$ . The equation of best fit was found to be  $\log k = (-0.45 \pm 0.05)\sqrt{I} - (0.25 \pm 0.03)$ .

The relationship between  $\log k$  and  $\sqrt{I}$  is linear and negative, so  $\log k$  decreases as  $\sqrt{I}$  increases. A least squares analysis of the graph of  $\log k$  vs.  $\sqrt{I}$  yields the linear regression shown in equation 8. Equation 9 is the Brønsted equation in which  $k$  is the rate constant,  $k_0$  is the rate constant of the reaction when the ionic strength is zero,  $z_1z_2$  is the charge of the transition state complex,  $A$  is the Debye-Hückel constant (0.509), and  $I$  is the ionic strength. Equations 8 and 9 can be related to determine  $k_0$ , and  $z_1z_2$ . The rate constant at zero ionic strength was determined to be  $0.56 \pm 0.04 M^{-1} s^{-1}$  and  $-0.44 \pm 0.05$  was the determined charge of the transition state complex.

$$\log k = (-0.45 \pm 0.05)\sqrt{I} - (0.25 \pm 0.03) \quad (8)$$

$$\log k = \log k_0 + 2Az_1z_2\sqrt{I} \quad (9)$$

## Conclusion

For the reaction between sodium bisulfite and potassium iodate, it was observed that, as ionic strength increased, the total reaction time also increased. As well, the rate constant,  $k$ , for

the reaction decreased with increasing ionic strength; thus, the graph of  $\log k$  as a function of  $\sqrt{I}$  is inversely linear. The negative slope of this graph results in a negative  $z_1z_2$  value, so the transition state complex is formed from ions with opposite charges. As a result, the transition state has a lower charge than the reactants and is, therefore, less stabilized by ionic strength than the reactants. For this reason the reaction is slower at high ionic strength.<sup>2</sup>

A source of error from this procedure is timing the reaction. For reliable and reproducible results, the stopwatch must be started and stopped at the same instance for each trial and reaction. A more reliable timing method would improve the accuracy of these results. One method would be continuously monitoring the progress of the reaction by observing the change in concentration, of a reactant or product, over time.

## References

1. Huffman, C. *Reaction Rate vs. Ionic Strength*. Western Carolina University. 2015
2. Atkins, P.; de Paula, J. *Physical Chemistry for the Life Sciences*. Second Edition. W.H. Freeman and Company, New York. 2006