

# The Kinetics of the Bromate-Bromide Reaction

This laboratory exercise was developed by modification of a kinetic method for the determination of phenols,<sup>1</sup> with the emphasis on the kinetic rather than on the analytical aspects. The original method was modified as follows: (1) the reagents were prepared in separate solutions, so that the concentration of each could be varied independently in the final reaction mixture; (2) perchloric acid was used in place of sulfuric acid, so that the hydrogen ion concentration could be accurately known.

The rate equation is of the form

$$-\frac{d[\text{BrO}_3^-]}{dt} = k[\text{BrO}_3^-]^2[\text{Br}^-]^2[\text{H}^+]^2$$

The method enables the three exponents to be evaluated separately and rate constants to be found for several temperatures. Hence the activation energy may be found from the Arrhenius equation.

If sulfuric acid replaces perchloric acid, the effect of the incomplete dissociation of the bisulfate ion may also be observed. The equipment required is simple—a stopwatch, a thermostat water bath, and ordinary glassware. If stock solutions are supplied, two students working as a team can comfortably complete all the measurements in two three-hour laboratory periods.

## Theoretical Basis

The stoichiometric equation for the reaction is



If a small concentration of phenol is present, it is mono-brominated very rapidly, so that the free bromine concentration is kept to a very low value, and a steady state concentration for bromine may be assumed.



The rate constant for this reaction at 25°C was found by Burgess and Latham<sup>2</sup> to be  $6.5 \times 10^6 \text{ l mole}^{-1} \text{ sec}^{-1}$ , about a million times faster than the formation of bromine. Thus, until monobromination of the phenol is completed, the bromine concentration remains very low, and methyl orange present in the solution is bleached only slightly. When monobromination is complete, dibromination begins at a slower rate, due to de-activation of the aromatic nucleus by the first bromine substituent. The rate constant for bromination of *o*-bromophenol is about one half, and for *p*-bromophenol, one hundredth of the value for the monobromination of phenol.<sup>2</sup> The slower rate of uptake of bromine when dibromination begins permits the free

bromine concentration to rise sharply to a value at which methyl orange is suddenly bleached. The time taken to bleach the dyestuff can be measured with a precision of about  $\pm 1$  sec. Since the reaction of one mole of bromate ion supplies bromine for the monobromination of three moles of phenol, the decrease in bromate ion concentration up to the time of bleaching can be evaluated.

If the ratio of the initial concentrations of phenol and bromate ion is kept small, less than 0.1, the rate of reaction falls off nearly linearly up to the time of decolorization, and the average rate of reaction  $-\Delta[\text{BrO}_3^-]/t$  may be taken as the initial rate  $-d[\text{BrO}_3^-]/dt$ . Further, detailed consideration of the concentration changes of the reactants as the reaction proceeds shows that the change in rate will depart least from linearity if the initial concentrations of reactants are in the ratio

$$[\text{BrO}_3^-]:[\text{Br}^-]:[\text{H}^+] = 1:2:3$$

This is the ratio in which the reactants are consumed in the reaction mixture.

## Safety Note

It is undesirable for concentrated perchloric acid and phenol to be used together in the same area. For this reason the perchloric acid was diluted to nearly 0.5 *M* before being issued to students for standardization. The standardization and mixing of the diluted perchloric acid with other reagents produced no difficulties or untoward reactions. In some instances, perchloric acid-phenol mixtures at concentrations of 0.3 *M* acid and 0.013 *M* phenol stood for several hours at room temperature without reaction. At a final test, such a mixture was kept at 100°C for an hour without reaction.

There therefore appears to be no hazards in using the dilute perchloric acid and phenol together.

## Experimental Details

Aqueous stock solutions of the following reagents were prepared

- 0.333 *M* potassium bromate
- 0.667 *M* potassium bromide
- 0.500 *M* perchloric acid
- 0.030 *M* phenol
- 0.500 *M* sodium nitrate
- 0.250 *M* sulfuric acid
- Methyl orange solution—40 mg of the sodium salt/liter

Analytical reagent grade chemicals were used without further purification. The perchloric and sulfuric acid solutions were standardized against dried anhydrous sodium carbonate, using methyl orange indicator.

Two sets of solutions were then prepared; the bromate-bromide mixtures, and the perchloric acid-phenol-methyl orange mixtures. The bromate-bromide mixtures contained 5.0 or 10.0 ml

<sup>1</sup> BURGESS, A. E., AND LATHAM, J. L., *Analyst*, **91**, 343 (1966).

<sup>2</sup> BURGESS, A. E., AND LATHAM, J. L., *J. CHEM. EDUC.*, **46**, 370 (1969).

aliquots of the stock solutions, and to them were added sufficient 0.5 M sodium nitrate solution to bring the ionic strength of the final reaction mixture to a value of 0.30, and sufficient water to bring the volume of the final reaction mixture to 50.0 ml in all cases. The second set of solutions contained 10.0 or 20.00 ml aliquots of the perchloric acid stock solution, 5.0 ml aliquots of the methyl orange solution, and aliquots of 0.03 M phenol solution ranging from 2.0 to 15.0 ml. This gave initial phenol concentrations in the reaction mixture ranging from 0.0012 to 0.0090 M.

### Determination of the Exponents of the Rate Equation

Four pairs of solutions were prepared, with the concentration of each reactant doubled in turn (see Table 1).

**Table 1.** Times for the Reaction of 0.002 mole liter<sup>-1</sup> of Bromate Ion, with Different Initial Concentrations of Reactants, at 25°C and an Ionic Strength of 0.30

	Initial [BrO <sub>3</sub> <sup>-</sup> ]	Initial [Br <sup>-</sup> ]	Initial [H <sup>+</sup> ]	Time (sec)
(1)	0.0333	0.0667	0.100	42.6
(2)	0.0333	0.133	0.100	21.5
(3)	0.0667	0.0667	0.100	21.1
(4)	0.0333	0.0667	0.200	10.7

The solutions, contained in 50 ml Nessler tubes, were brought to the thermostat temperature (25° ± 0.5°C). The tube containing the acid-phenol-methyl orange mixture was supported over a white tile in the water bath. The bromate-bromide mixture was added quickly, and the stopwatch started. Uniform mixing was ensured by a brief stirring. The indicator color was observed longitudinally, and the watch stopped when the last tinge of color disappeared.

The phenol concentration in each tube was 0.006 M, so that the change in bromate ion concentration up to decolorization time was 0.002 mole liter<sup>-1</sup> for all cases. The results are summarized in Table 1. The times are mean values of three measurements in all cases, and in no case did the times for replicate runs differ by more than 0.5 sec.

For all runs

$$-\Delta[\text{BrO}_3^-]/t \simeq -d[\text{BrO}_3^-]/dt = k[\text{BrO}_3^-]^x[\text{Br}^-]^y[\text{H}^+]^z$$

For runs (3) and (1), we have

$$\frac{0.002/21.1}{0.002/42.6} = \frac{k(0.0667)^x(0.0667)^y(0.100)^z}{k(0.0333)^x(0.0667)^y(0.100)^z} = 2^x = \frac{42.6}{21.1} = 2.02$$

Hence, within the limits of experimental error,  $x = 1$ . Similarly,  $2^y = 42.6/21.5 = 1.98$ , and  $y = 1$ .  $2^z = 42.6/10.7 = 3.98$ , and  $z = 2$ . The complete rate equation is therefore

$$-\frac{d[\text{BrO}_3^-]}{dt} = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$$

### The Rate Constant at Various Temperatures and the Energy of Activation

For these measurements, bromate-bromide solutions and perchloric acid-methyl orange solutions were prepared so that the initial concentrations were as given in line (1) of Table 1. Water and sodium nitrate were added to make the volume of the reaction mixture 50.0 ml and its ionic strength 0.30.

For the runs at 0° and 7°C, aliquots of 2, 4, 6, 8, 10 ml of 0.03 M phenol solution were added to the per-

chloric acid solutions. These additions gave initial phenol concentrations ranging from 0.0012 to 0.0060 mole liter<sup>-1</sup> in steps of 0.0012 mole liter<sup>-1</sup>. For the runs at 15°, 20°, 25°, and 30°C, the aliquots of phenol solution were made 3, 6, 9, 12, and 15 ml giving initial phenol concentrations from 0.0018 to 0.0090 mole liter<sup>-1</sup> in steps of 0.0018 mole liter<sup>-1</sup>.

The higher phenol concentrations were used at the higher temperatures so that the times required for decolorization were long enough to measure with reasonable accuracy under conditions giving more rapid reaction.

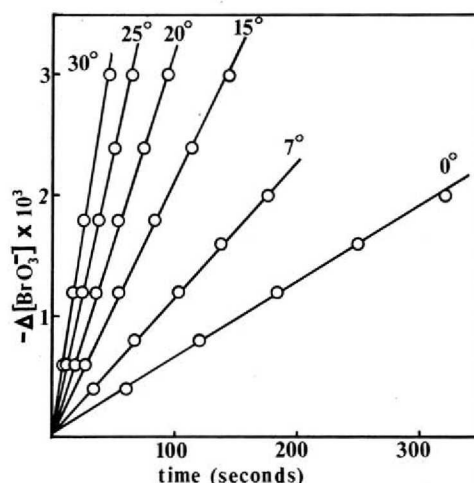
Each set of tubes was brought to temperature in the water bath, the reagents mixed, and the time taken to decolorize the methyl orange measured as before.

The rate of reaction for each tube is given by  $-\Delta[\text{BrO}_3^-]/t$ , and  $-\Delta[\text{BrO}_3^-]$  is obtained from one third of the phenol concentration in each case. If  $a$  = initial bromate concentration, then the reaction rate is

$$-\frac{d[\text{BrO}_3^-]}{dt} \simeq \frac{-\Delta[\text{BrO}_3^-]}{t} = k(a \times 2a \times (3a)^2) = 18ka^4$$

where  $2a$  is the initial bromide, and  $3a$  the initial hydrogen ion concentration. Therefore  $-\Delta[\text{BrO}_3^-] = 18ka^4t$ .

A plot of  $-\Delta[\text{BrO}_3^-]$  against  $t$  should be linear, with a slope of  $18ka^4$ . For these measurements,  $a = 0.0333$ , and hence  $k$  can be evaluated. The plots for six temperatures are shown in Figure 1. The lines of best fit



**Figure 1.** The change in bromate ion concentration with time at various temperatures in the reaction  $\text{BrO}_3^- + 5\text{Br}^- + 6\text{H}^+ \rightarrow 3\text{Br}_2 + 3\text{H}_2\text{O}$ .

were calculated by the method of least squares, and the linear correlation coefficients are better than 0.999 for all lines.

No correction for bleaching time at zero phenol concentration was made. At all temperatures above 0°C, the correction was shorter than the time of mixing, and at 0°C, it was between 1 and 2 sec. The fact that all the lines cut the time axis at a negative time shows that the timer was stopped prematurely. This subjective error is difficult to avoid, but providing its value is consistent for all measurements, it should not affect the slope of the lines.

The slopes and the rate constants calculated from them are shown for each temperature in Table 2. When these values are plotted according to the Arrhenius equation

Table 2. Slopes of the Plot  $-\Delta[\text{BrO}_3^-]$  versus  $t$ , and Rate Constants for the Reaction  $-\Delta\text{BrO}_3^- + 5\text{Br}^- + 6\text{H}^+ \rightarrow 3\text{Br}_2 + 3\text{H}_2\text{O}$ , at an Ionic Strength of 0.30, and Various Temperatures

$t^\circ\text{C}$	Slope (mole liter <sup>-1</sup> sec <sup>-1</sup> )	$k$ (mole <sup>-2</sup> liter <sup>2</sup> sec <sup>-1</sup> )
0	0.00615	0.277
7	0.0113	0.507
15	0.0203	0.915
20	0.0315	1.420
25	0.0450	2.025
30	0.0631	2.842

$$\log k = \frac{-E}{2.303R} \cdot \frac{1}{T} + \text{constant}$$

the graph shown in Figure 2 is obtained. The energy of activation evaluated from the slope of this graph is 12,900 cal/mole of bromate ion reacted.

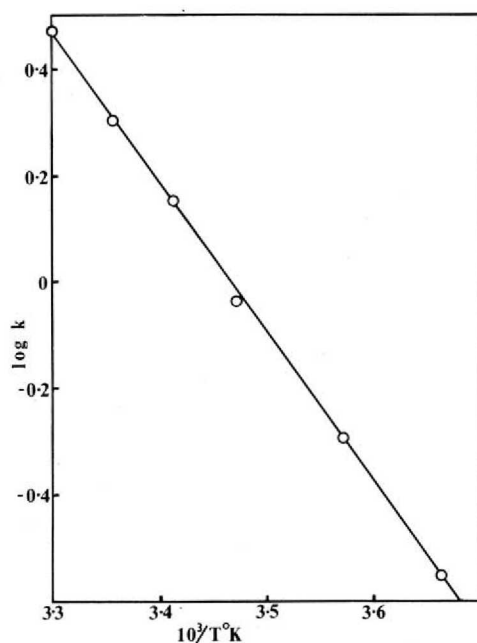


Figure 2. The logarithm of rate constant plotted against reciprocal temperature for the reaction  $\text{BrO}_3^- + 5\text{Br}^- + 6\text{H}^+ \rightarrow 3\text{Br}_2 + 3\text{H}_2\text{O}$ .

### The Reaction in the Presence of Sulfuric Acid

The rate of the reaction was measured under the same conditions as for runs (1) and (4) of Table 1, except that 0.100 *M* perchloric acid was replaced by 0.050 *M* sulfuric acid for run (1), and 0.200 *M* perchloric acid was replaced by 0.100 *M* sulfuric acid for run (4). The time required for 0.002 mole liter<sup>-1</sup> of bromate ion to react increased from 42.6 to 72.6 sec for the first case, and from 10.7 to 22.1 sec for the second. The exponent of the hydrogen ion concentration in the rate equation calculated from these times has a value of 1.7. Acceptance of this value would imply that there was some difference in the mechanism of the reaction in the presence of ions derived from sulfuric acid. Bray and Liebhafsky<sup>3</sup> have shown that there are no grounds for the acceptance of this supposition.

It is therefore possible in principle to solve the rate equation for the unknown hydrogen ion concentration

and by means of charge and mass balance equations to find the equilibrium concentrations of sulfate and bisulfate ions. The activity coefficient of the sulfate ion calculated from the known ionic strength of the solution then permits the dissociation constant of the bisulfate ion to be found. The value obtained in this way was  $8 \times 10^{-3}$  mole liter<sup>-1</sup>, about one half of the accepted value of  $1.2 \times 10^{-2}$  mole liter<sup>-1</sup>. An error of 10% in the hydrogen ion concentration would produce a discrepancy of about this size in the value of  $K_{\text{HSO}_4^-}$ . Since the rate constant of the bromate-bromide reaction varies considerably with ionic strength,<sup>3</sup> and the ionic strength of the reaction mixture containing sulfuric acid is lower than that containing perchloric acid, the calculation of the unknown hydrogen ion concentration using a rate constant determined at an ionic strength of 0.30 is not strictly valid.

Nevertheless, the results are clear evidence of the incomplete dissociation of sulfuric acid, and this extension of the exercise was thought to be worthwhile. At 0°C, the apparent order with respect to hydrogen ion is 1.5, indicating a lower degree of dissociation at the lower temperature.

### Other Observations

A few minutes after the completion of the monobromination of the phenol, signaled by decolorization of the methyl orange, a pale, cream-colored precipitate was observed to form slowly throughout the solution. This was presumably the dibrominated phenol. When the tubes were left undisturbed during this stage, the liquid gelled sufficiently firmly for the tube to be held horizontally without the gel breaking. The gels were firmer with higher phenol concentrations, but the phenomenon occurred even at the lowest phenol concentrations used. Considering the very low concentration of  $1.2 \times 10^{-3}$  molar, the structure of these gels should be of interest.

Following the appearance of the pale colored precipitate, a somewhat darker yellow product appeared, presumably the tribromophenol, and ultimately free bromine appeared.

### Conclusion

In writing reports of the exercise, students are asked

- to comment critically on the analytical application, and to suggest other readily brominated organic compounds which might be determined similarly
- to explain why the determination of *m*-cresol is not possible by this method
- to suggest other methods of detecting the completion of monobromination, not open to subjective errors (spectrophotometric and potentiometric methods are both feasible)
- to justify the choice of the 1:2:3 ratio for the reactant concentrations

The exercise is well received by students, and may be presented in the form of a genuine investigation, especially that part of it concerned with the apparent difference in order with respect to hydrogen ion when different acids are used. Other acids of intermediate strength, e.g., the chloracetic acids could probably be used providing there was no direct reaction with components of the reaction mixture.

Since the exercise has aspects of analytical, physical, and organic chemistry, it is seen as valuable in helping

<sup>3</sup> BRAY, W. C., AND LIEBHAFSKY, H. A., *J. Amer. Chem. Soc.*, 57, 51 (1935).

to break down the mythical boundaries between these areas in the students' minds.

I should like to thank my colleagues for useful dis-

cussions, my students for carrying out many trial runs, and the computer staff of this Institute for the least squares calculations.



Rappel :  $\text{BrO}_3^- / \text{Br}_2$  : 1,5 V

$\text{Br}_2 / \text{Br}^-$  : 1,08 V

Détermination des ordres par rapport à  $\text{BrO}_3^-$  ,  $\text{Br}^-$  ,  $\text{H}^+$  :

Pour cela, on réalise 4 expériences. Pour chacune d'elles, on prépare 2 béchers, le bécher n°1 et le bécher n°2 dont les compositions sont indiquées sur les tableaux n°1 et n°2 ci-dessous : ( les volumes sont en mL )

Bécher n° 1	$\text{KBrO}_3$ 0,333 M	KBr 0,667 M	$\text{NaNO}_3$ 0,5 M	Eau distillée
Expérience 1	5	5	10	5
Expérience 2	5	10	3,33	6,67
Expérience 3	10	5	6,67	3,33
Expérience 4	5	5	0	5

Tableau n°1

Bécher n° 2	$\text{HClO}_4$ 0,5 M	phénol 0,030 M	hélianthine 40 mg / L
Expérience 1	10	10	5
Expérience 2	10	10	5
Expérience 3	10	10	5
Expérience 4	20	10	5

Tableau n°2

A  $t = 0$  on mélange les béchers 1 et 2 : le volume total fait alors 50 mL et la force ionique vaut 0,3 .

Exemples de résultats ( à la température du laboratoire : 18° C )

Expérience 1 : 1 minute et 10 secondes

Expérience 2 : 37 secondes

Expérience 3 : 34 secondes

Expérience 4 : 17 secondes

Pour l'énergie d'activation , on refait l'expérience 1 à 2 ou 3 températures .

Exemple : expérience 1 refaite à 3° C : il faut 3 minutes et 46 secondes pour décolorer l'hélianthine .