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Title: A STUDY OF THE KINETICS AND MECHANISM OF PERBROMATE-BROMIDE OXIDATION-REDUCTION REACTION

Abstract approved: Alfred J Ericson

The goal of this research project was to study the perbromate-bromide oxidation-reduction reaction.

Earlier studies have indicated perbromate is quite sluggish in its reaction. This inertness of the perbromate ion stands in sharp contrast to its high thermodynamic oxidizing power which is greater than that of any other oxyhalite ion that exist in aqueous solution.

The reaction of perbromate ion with a number of two-equivalent reductants have been studied in aqueous solution at an ionic strength of approximately one.

This research investigated the kinetics of the perbromate-bromide reaction. Oxygen transfer from perbromate to bromide may be the key step in the mechanism of this reaction. Experiments were carried out at $[H^+] = 0.25 \times 10^{-2} - 1.00 \times 10^{-2}$ M, temperature at 326.7, 331.2, 336.2 and 341.2 K and a constant ionic strength of 0.20 adjusted with $NaClO_4$. The rate law

$$d[Br_3^-]/dt = k[BrO_4^-][Br^-]^2[H^+]^2$$

was confirmed. From the rate law, rate constants at several temperatures were calculated and the activation energy was determined to be 16.8 Kcal/mol. The results were also compared to the data of analogous oxyhalite reactions from both experiment and literature.

The kinetic salt effect was also investigated by comparing rates at several different ionic strengths varying from 0.10 to 0.50 M. The results were consistent with the Bronsted-Bjerrum relationship and the Debye-Huckel constant is -0.41.

A STUDY OF THE KINETICS AND MECHANISMS OF PERBROMATE-BROMIDE OXIDATION-REDUCTION REACTION

A Thesis
Presented to
the Division of Mathematical & Physical Sciences
Emporia State University

In Partial Fulfillment
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by
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CHAPTER I

INTRODUCTION

It has been two decades since the first successful preparation of the perbromate species [1,2]. Previous studies have indicated perbromate is quite sluggish in reaction, although the perbromate is not as inert as perchlorate [3].

The inertness of the perbromate ion stands in sharp contrast to its high thermodynamic oxidizing power [4], which is greater than that of any other oxyhalide ion that exists in aqueous solution. Recent studies of perbromate reacting with azide, chlorite, nitrite and iron (II) complex show that perbromate reacts slowly with a wide range of reductants [5,6].

This study has investigated the kinetics and mechanisms of the perbromate-bromide reaction. Oxygen transfer from perbromate to reductant has been proposed as a key step in the mechanism of the reaction for several reductants [5].

Bromide, a two-electron reductant, reduces perbromate in acidic solution and at constant ionic strength solution according to the reaction

$$BrO_4^- + 7Br^- + 8H^+ \longrightarrow 4Br_2 + 4H_2O \qquad (1)$$

The purpose of this investigation was to provide kinetic data for the oxygen transfer reduction process of perbromate. The kinetics of the perbromate-bromide reaction were studied by following the formation of the tribromide ion with a EU-700 GCA/McPherson uv-visible Spectrophotometer at the wavelength of 275 nm to monitor the rate of the reaction. The Initial Rate Method (IRM) was used to analyze kinetic data for the reaction. The reaction rate constant and the activation energy of the reaction were determined.

The results of the experiments were compared with experimental data and literature values of two analogous oxyhalide reactions, i.e. the bromate-bromide reaction [7,8,9] and the periodate-iodide reaction [10].

The kinetic salt effect was also investigated by comparing the rate constants at various ionic strengths from 0.10 to 0.50 M. The results were plotted as log k/k_0 vs. $I^{1/2}$ and interpretated by the Bronsted-Bjerrum relationship [11,12].

CHAPTER II

EXPERIMENT SECTION

The procedures of preparation and recrystallization of perbromate has been previously described in the literature [3,13,14]. The material made was dried to constant weight in a drying oven at 110° C before it was analyzed. The samples were thermally decomposed to KBr at 480° C in a covered porcelain crucible. The thermal decomposition of perbromate to bromide and oxygen proceeds in two steps.

1. Decomposition of perbromate to bromate at 275° C.
2. Decomposition of bromate to bromide at 390° C.

The residue was dissolved in water and titrated with standard silver nitrate solution using dichlorofluorescein as an indicator. The weight loss during decomposition was taken as a measure of the oxygen content of the sample [3,14]. The analysis of our perbromate samples are listed in Table 1.

The rate of the reaction was measured spectrophotometrically by following the rate of the formation of Br_2. In the presence of excess bromide ion, the tribromide species (Br_3^-) was formed and the absorbance was measured at 275 nm. The molar absorptivity of tribromide at this wavelength is 3.5 x 10^4 [3]. When an excess of bromide is not present, the appearance of bromine (Br_2) can be monitored at its absorption maxima 395 nm, with a molar absorptivity of 160. Appropriate initial concentrations were chosen so that the

TABLE 1

Perbromate Purities Determination

SAMPLE #	1	2	3	4
Wt of sample/g	.7538	.4228	.4240	.4062
Wt of oxygen in sample/g	.2254	.1286	.1300	.1262
Calc. formula $KBrO_x$, X =	3.17	3.25	3.28	3.35
ml of .0280N $AgNO_3$ for 1/10 sample	16.10	8.85	9.60	9.10
millimole KBr in sample	4.51	2.48	2.69	2.55
millimole O in sample	14.1	8.04	8.13	7.89
Exp. formula $KBrO_x$, X =	3.12	3.24	3.02	3.10

X = 3.26 ± 0.07 based on weight loss.

X = 3.12 ± 0.09 based on titration.

calculation were convenient.

The concentrations of bromide and perbromate were varied in the range from 5.00×10^{-3} to 2.00×10^{-2} mol/dm^3 and 1.0×10^{-4} to 4.0×10^{-4} mol/dm^3, respectively, and all individual rate constants were obtained from the average of at least three determinations.

The ionic strength was maintained constant at 0.20 with addition of 0.50 M $NaClO_4$. In kinetic studies, the perchlorate ion is frequently employed to adjust the ionic strength because of its chemical stability, poor complexing and ion-associaton properties.

PHYSICAL MEASUREMENTS

Uv-vis spectra and the kinetic experiments were recorded on a GCA/McPherson uv-visible spectrophotometer. The reactions were slow enough to permit the change of absorbance with time data to be recorded on a GCA/McPherson EU-205-11 strip chart recorder. The chart speed was set at 1 cm per minute. In the mean time, absorbance reading were recorded and analyzed by a linear least-squares fitting computer program to obtain the slope as a measure of the initial rate of the reaction. A standard R-372 photomultipler tube was used as the detector.

A 10 cm optic cylindrical cell with a water jacket and a Haake FS model bath circulator were employed in order to maintain constant temperature. The measurements were run at 326.7, 331.2, 336.2, and 341.2K.

The reactants were mixed first, excluding the perchloric acid, and brought to the required temperature in the constant temperature bath. Then the required amounts of perchloric acid were quickly pipetted into the volumetric bottle which contained premixed reductants. After fast mixing, the reaction mixture was transferred rapidly to the thermostated cell and the course of the reaction was followed by the change of the absorbance of tribromide, Br_3^- at 275 nm. The molar absorptivities of the perbromate and the other product, water, are very low compare to that of tribromide at 275 nm. Unreacted perbromate did not interfere with the analysis, nor would other reactants or products.

REAGENTS

Perbromate was synthesized as described in earlier literature [3,13,14]. It was obtained by oxidation of bromate in alkaline aqueous solution. The most practical synthesis involves oxidation with elemental fluorine in a sodium hydroxide solution. The stock perbromate solution was prepared after the material was dried to constant weight in a drying oven at 110° C. The reaction solutions were prepared by mixing the perbromate and bromide solutions in several ratios, $[BrO_4^-]/[Br^-]$, from 0.01 to 0.04 with 0.50 M $HClO_4$ as H^+ source, pH range from 2.0 to 2.6 at ionic strength, I, equal to 0.20 adjusted with $NaClO_4$.

All stock solutions were prepared by dilution of reagent-grade materials or the prepared potassium perbromate with distilled water. The concentration of the stock sodium perchlorate was 0.500 M, stock perchloric acid was 0.500 M, stock potassium bromide was 0.100 M and potassium perbromate stock solution was 5.00×10^{-2} M.

KINETICS

The rate law of the reaction was investigated by the following procedure; one reactant was varied in concentration while other factors were held constant. The concentration of the product, Br_3^-, was determined spectrophotometrically at 275 nm. The order for the reactant was evaluated from a plot of logarithm of reaction rate against the logarithm of the varied concentration. When the order with respect to each of the three reactants has been determined, the rate law can be written.

DATA PROCESSING

Kinetic results were fitted by a linear and a nonlinear least-squares curve fitting computer programs to the integer order rate equation. Activation parameters and their uncertainties were obtained from a linear least-squares treatment of the temperature variation of the rate constant.

CHAPTER III

RESULTS

THE RATE LAW FOR PERBROMATE-BROMIDE REACTION

First, the observed absorbances, A_{obsd}, were plotted against reaction time and extrapolated to the time of mixing when the reaction started to obtain the initial absorbance. Absolute absorbances were calculated and using Beer's Law, each absolute absorbance was used to calculate the generation rate of bromine. When excess bromide ion is present, the product, bromine, is bonded with it and monitored as tribromide (Br_3^-) at a wave length of 275 nm. Beer's Law is

$$\text{Absorbance} = A_{obsd} - A_0 = a \times b \times c$$

where a is molar extinction constant, for tribromide at 275 nm is 3.5×10^4 $cm^{-1}M^{-1}$ [3], b is cell length in cm and c is concentration of the substance under study in mole/dm^3.

The detailed results of the study of the rate law of the reaction between perbromate and bromide in aqueous perchloric acid are listed in Table 2 - 5. The reactions were studied as a function of initial perbromate ion, bromide ion, and perchloric acid concentration. In all experiments, there was an excess of bromide present, so that complete reduction of oxidizing agent occurred and the tribromide ion formed could be monitored.

Analysis of the results indicated that at constant perchloric acid concentration the kinetic data were consistent with a fifth-order rate law equation, first order with respect to perbromate and second order with respect to both bromide ion and hydrogen ion concentrations. These orders were confirmed by the fact that linear relationships were obtained when the logarithm of the reaction rate were plotted against the logarithm of the reaction concentration. The results of the kinetic experiments designed to determine the order of the reaction are summarized in Table 2 - 5. The data, listed in Table 6, 7, and 8, were analyzed by means of a linear least squares curve fitting computer program [15] in order to obtain the reaction orders with respect to each of the reactions. The determined values of the reaction orders are also listed in Table 6 - 8 and the rate law deduced as follow

$$\text{Rate} = k[BrO_4^-][Br^-]^2[H^+]^2 \quad (2)$$

THE EFFECT OF BROMIDE ION

Experiments were carried out in triplicate with 0.020 M perbromate, 5.00×10^{-3} - 2.00×10^{-2} M bromide, 0.50×10^{-2} M $HClO_4$, at an ionic strength of 2.00×10^{-1} M, and at temperatures of 326.7, 331.2, 336.2, and 341.2 K, to discern the effect of bromide ion on the rate of the reaction. The effect of the bromide ion concentration of apparent second order was confirmed and

TABLE 2

Reaction Rate of the Perbromate-Bromate Reaction at I = 0.2, 326.7 K

$10^4[BrO_4^-]$ M	$10^2[Br^-]$ M	$10^2[H^+]$ M	Rate$\times10^{10}$	k
1.00	1.00	0.50	1.9	740
2.00	1.00	0.50	4.0	800
3.00	1.00	0.50	6.8	910
4.00	1.00	0.50	8.6	857
2.00	0.50	0.50	1.6	(1272)
2.00	1.00	0.50	4.0	800
2.00	1.50	0.50	10.1	894
2.00	2.00	0.50	17.1	853
2.00	1.00	0.25	1.1	840
2.00	1.00	0.50	4.0	800
2.00	1.00	0.75	9.4	837
2.00	1.00	1.00	17.7	884

$k = 900 \pm 100$

TABLE 3

Reaction Rate of the Perbromate-Bromate Reaction at I = 0.2, 331.2 K

$10^4[BrO_4^-]$ M	$10^2[Br^-]$ M	$10^2[H^+]$ M	Rate$\times10^{10}$	k
1.00	1.00	0.50	3.2	1260
2.00	1.00	0.50	6.1	1210
3.00	1.00	0.50	8.9	1185
4.00	1.00	0.50	11.7	1165
2.00	0.50	0.50	2.3	(1872)
2.00	1.00	0.50	6.1	1210
2.00	1.50	0.50	15.9	1417
2.00	2.00	0.50	26.3	1315
2.00	1.00	0.25	1.5	1208
2.00	1.00	0.50	6.1	1210
2.00	1.00	0.75	14.1	1251
2.00	1.00	1.00	26.5	1323

k = 1300 ± 200

TABLE 4

Reaction Rate of the Perbromate-Bromate Reaction at I = 0.2, 336.2 K

$10^4[BrO_4^-]$ M	$10^2[Br^-]$ M	$10^2[H^+]$ M	Rate$\times10^{10}$	k
1.00	1.00	0.50	4.6	1848
2.00	1.00	0.50	8.8	1754
3.00	1.00	0.50	11.5	1529
4.00	1.00	0.50	16.5	1647
2.00	0.50	0.50	3.6	(2912)
2.00	1.00	0.50	8.8	1754
2.00	1.50	0.50	21.5	1909
2.00	2.00	0.50	35.8	1788
2.00	1.00	0.25	2.6	(2104)
2.00	1.00	0.50	8.8	1754
2.00	1.00	0.75	20.5	1825
2.00	1.00	1.00	38.8	1938

$k = 1900 \pm 400$

TABLE 5

Reaction Rate of the Perbromate-Bromate Reaction at I = 0.2, 341.2 K

$10^4[BrO_4^-]$ M	$10^2[Br^-]$ M	$10^2[H^+]$ M	Rate$\times 10^{10}$	k
1.00	1.00	0.50	7.3	2896
2.00	1.00	0.50	13.1	2616
3.00	1.00	0.50	18.9	2513
4.00	1.00	0.50	24.1	2410
2.00	0.50	0.50	3.4	2736
2.00	1.00	0.50	13.1	2616
2.00	1.50	0.50	30.1	2678
2.00	2.00	0.50	48.0	2399
2.00	1.00	0.25	4.0	(3216)
2.00	1.00	0.50	13.1	2616
2.00	1.00	0.75	30.1	2673
2.00	1.00	1.00	50.3	2516

k = 2700 ± 200

TABLE 6

Reaction Rates at Constant Bromate and Perchloric Acid Concentrations[a]

Temperature K	$10^4[BrO_4^-]$ M	10^{10} x Rate M/sec	Rex. Order
326.7	0.50	1.9	
	1.00	4.0	
	1.50	6.8	
	2.00	8.6	1.1
331.2	0.50	3.2	
	1.00	6.1	
	1.50	8.9	
	2.00	11.7	0.9
336.2	0.50	4.6	
	1.00	8.8	
	1.50	11.5	
	2.00	16.5	0.9
341.2	0.50	7.3	
	1.00	13.1	
	1.50	18.9	
	2.00	24.1	0.9

Reaction Order = 1.0 ± 0.1

a. $[Br^-] = 1.00 \times 10^{-2}$ M, $[H^+] = 0.50 \times 10^{-2}$ M for all runs listed in this table and the ionic strength maintained at 0.20 M.

b. The reaction order with respect to perbromate shown above is a first order reaction.

TABLE 7

Reaction Rates at Constant Bromate and Perchloric Acid Concentrations[a]

Temperature K	$10^3[Br^-]$ M	10^{10} x Rate M/sec	Rex. Order
326.7	0.50	1.6	
	1.00	4.0	
	1.50	10.1	
	2.00	17.1	1.7
331.2	0.50	2.3	
	1.00	6.1	
	1.50	16.0	
	2.00	26.3	1.8
336.2	0.50	3.3	
	1.00	8.8	
	1.50	21.5	
	2.00	35.0	1.7
341.2	0.50	3.4	
	1.00	13.1	
	1.50	30.0	
	2.00	48.0	1.9

Reaction Order = 1.8 ± 0.1

a. $[BrO_4^-] = 2.00 \times 10^{-4}$ M, $[H^+] = 0.50 \times 10^{-3}$ M for all runs listed in this table and the ionic strength maintained at 0.20 M.

b. The reaction order with respect to bromide shown above may refer to a whole number of two.

TABLE 8

Reaction Rates at Constant Perbromate and Bromide Concentrations[a]

Temperature K	$10^2[H^+]$ M	10^{10} x Rate M/sec	Rex. Order
326.7	0.25	1.1	
	0.50	4.0	
	0.75	9.4	
	1.00	17.7	2.0
331.2	0.25	1.5	
	0.50	6.1	
	0.75	14.1	
	1.00	26.5	2.0
336.2	0.25	2.6	
	0.50	8.8	
	0.75	20.5	
	1.00	38.8	1.9
341.2	0.25	4.0	
	0.50	13.1	
	0.75	30.1	
	1.00	50.3	1.8

Reaction Order = 1.9 ± 0.1

a. $[BrO_4^-] = 2.00 \times 10^{-4}$ M, $[Br^-] = 1.00 \times 10^{-2}$ M for all runs listed in this table and the ionic strength maintained at 0.20 M.

b. The reaction order with respect to hydrogen ion shown above may refer to a whole number of two.

the results are listed in Table 7. The rate constants, k, were calculated from the derived rate law and were determined to be 1000 ± 200, 1500 ± 300, 2000 ± 600, and 2600 ± 100 at 326.7, 331.2, 336.2, and 341.2 K, respectively.

THE EFFECT OF HYDROGEN ION

Most oxidation-reduction reactions of oxyanions exhibit a first- or second-order hydrogen ion dependence. Therefore, in this research the reaction was investigated at varying hydrogen ion concentrations.

The effect of pH was studied with composite solutions of perbromate at various hydrogen ion concentrations. The effect of the hydrogen ion concentration on the apparent second-order rate constant was also investigated. Sodium perchlorate was used to maintain constant ionic strength, and the results are summarized in Table 8. The influence of hydrogen ion on the second-order rate was consistent with other perbromate reactions [5,6].

TEMPERATURE DEPENDENCE AND KINETIC DATA

At the investigated concentrations, the reaction is extremely slow when the temperature is 323.2 K or lower. A temperature of 326.7 K was chosen as the starting temperature for the kinetic studies.

Rate constants were determined at four different temperatures in the range from 326.7 to 341.2 K. The results of the reaction at these different temperatures are presented in Table 9.

The rate of reaction increases with an increase of temperature within the range of investigation. From the rate constant data in Table 9, a plot of log k vs. the reciprocal of absolute temperature, Figure 1, was generated. The data gave a linear Arrhenius plot from which an activation energy of 16.8 kcal/mol was derived. Using standard equations and Erying's absolute reaction rate theory [16]

$$k = (k_B/h) \times T \times \exp(\Delta S/R) \times \exp(\Delta H/RT)$$

where k_B is Boltzman's constant, h is Plank's constant, T is the temperature in kelvins, ΔS and ΔH are the entropy change and the enthalpy change for activation. Thermodynamic parameters were calculated at each different temperature and solving the Erying's equation. The value of activation enthalpy, activation free energy and activation entropy at 341.2K are 16.1 kcal/mol, 47.6 kcal/mol and -92.3 cal/mol.K, respectively.

The rate constants given in Table 9 are in terms of the rate equation (2) and apply to the rate of disappearance of perbromate.

TABLE 9

Influence of Temperature on Rate Constant

Temperature	k
326.7	900 ± 100
331.2	1300 ± 200
336.2	1900 ± 400
341.2	2700 ± 200

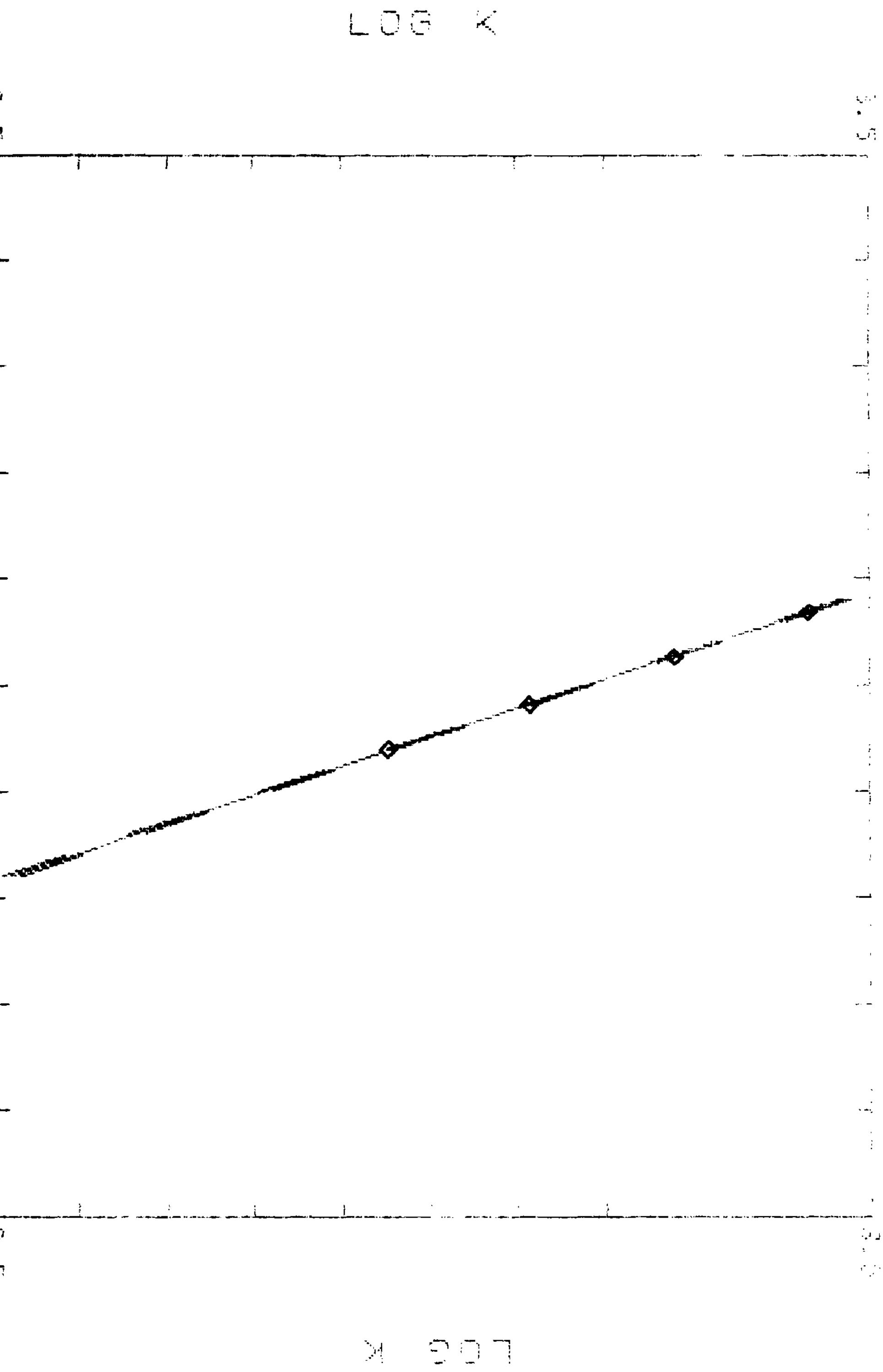
* Experiments were determined under the conditions

$[BrO_4^-] = 2.00\text{x}10^{-4}$ M

$[Br^-] = 1.00\text{x}10^{-2}$ M

$[H^+] = 1.00\text{x}10^{-2}$ M

Figure 1. Plot of log k verses 1000/T for the Perbromate-Bromide Reaction


LOG K
3.5
LOG K

EFFECT OF IONIC STRENGTH

Possible medium effects were investigated by the effect of ionic strength on the rate of reaction. Sodium perchlorate was used to adjust the ionic strength.

The effect of ionic strength on the apparent rate constants are summarized in Table 10. The rate of reaction decreases with an increase of the ionic strength, the charge product of perbromate ion, bromide ion and perchloric acid is negative sign [17], are consistent with an extended form of Debye-Huckel limiting law called the Bronsted-Bjerrum relationship, which is

$$\log k = \log k_0 + 2AZ_A Z_B I^{1/2}$$

predicts that a plot of log k/k_0 vs. $I^{1/2}$, Figure 2, would be linear with a slope equal $2AZ_A Z_B$ and an intercept, theoretically, of zero [11,12,18]. The rate constant k was found to be 1800, 1500, 1400, 1300, and 1200, $M^{-3}S^{-1}$ at ionic strengths of 0.10, 0.20, 0.30, 0.40, and 0.50, respectively, from the plot of log k vs. $I^{1/2}$. The constant k_0 was determined to be 3.4 and the Debye-Huckel constant equals to -0.41.

TABLE 10

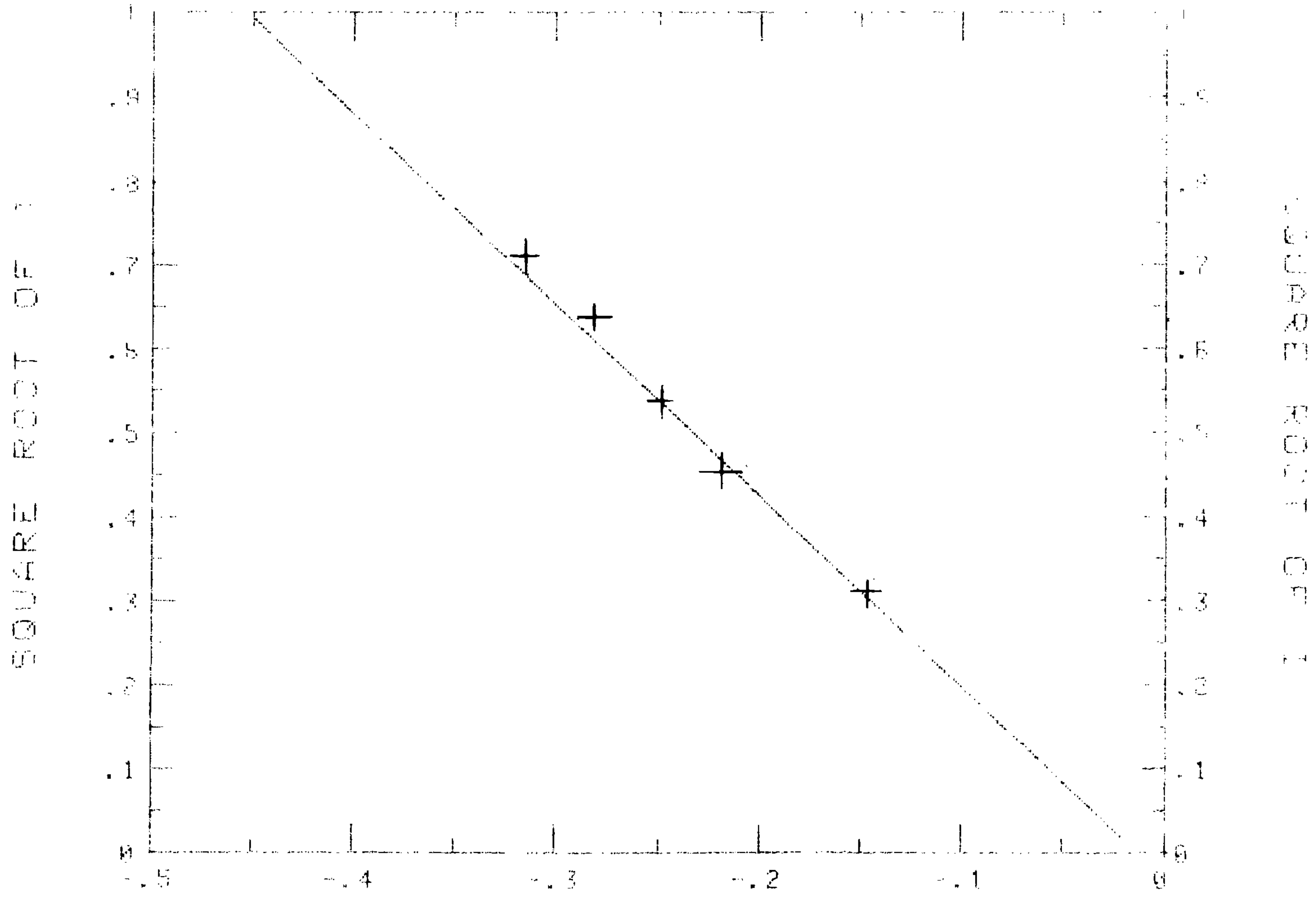
The Effect of Ionic Strength on The Perbromate-Bromide Oxidation-Reduction Raction

Ionic Strength M	Ratex10^{10} M/Sec	k
0.10	36.4	1800
0.20	30.8	1500
0.30	28.0	1400
0.40	26.2	1300
0.50	25.2	1200

Log k_0 = 3.4

A = -.41

Figure 2. Plot of log k/k_o verses Square Root of Ionic Strength


SQUARE ROOT OF I
SQUARE ROOT OF I
1
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
-.5
-.4
-.3
-.2
-.1
0

CHAPTER IV

DISCUSSION

The oxidation-reduction reaction is adequately described by the expression

$$\text{Rate} = d[Br_3^-]/dt$$

$$= k[BrO_4^-][Br^-]^2[H^+]^2$$

This rate law expression is similar to that of an analogous oxyhalide reaction, the periodate-iodide reaction, which is first-order with respect to periodate and iodide and second-order with respect to hydrogen ion [10].

Oxygen transfer may well be the most often encountered mechanism for oxidation by perbromate [5] but it may not be unique. The mechanism for the reduction of perbromate consists of transfer of one of the perbromate oxygen atom to the reductant. Most common reductants accept an oxygen atom from the oxidant. Most of the reactions of perbromate involve an inverse hydrogen ion dependence [5,6,19]. Most oxyhalide ions involve first or second order positive hydrogen ion dependence [5,7,8,10], which is because oxyhalide protons labilize the halate oxygen. Protons involved in the perbromate reaction will form a less basic species with reductants and will not accept an oxygen from perbromate. If the reductant does not accept a proton, the reaction will be independent of proton concentratin [5].

The proton has a second-order influence on perbromate and is found to be consistent with most oxyhalide ion reactions which involve two-electron reductants [5,7,8,10]. The profile for the second-order proton dependence rate law, shown in Table 9, suggests that the protonation of reductant is the favorite path for the reaction of equation (1). Because the perbromate entered the reactions as a tetrahedral oxyanion [3,5], it did not form an activated complex with the proton. The hydrogen dependence in this reaction may be attributed to the characteristics of the reductant [5,10,19].

By combing the standard redox potential for the perbromate/bromate (-1.763 V) [20], bromate/bromine (1.44 V), and bromide/bromine (-1.087 V) couples, Table 11, one find that the perbromate-bromide reaction has a standard potential of -1.410 V, which corresponds to a value of 260 kcal/mol for the standard Gibb's free energy.

The perbromate ion was only slowly reduced in the reaction, indicating the presence of a high activation barrier between Br^- and Br(VII). This high activation barrier plus the fairly high electrode potential could account for the difficulties encountered in the synthesis of the perbromate compound.

Scaife and Jyrell [21] found that the bromine generated in a reaction will establishes a equilibrium with bromide in the solution

$$Br_2 + Br^- \quad <=====> \quad Br_3^- \qquad K$$

where the equilibrium constant, K, equal to k/k', has a

TABLE 11

Summation of Half Reactions

	E^o
$BrO_4^- + 2H^+ + 2e^- \longrightarrow BrO_3^- + H_2O$	-1.763 V
$BrO_3^- + 6H^+ + 6e^- \longrightarrow Br^- + 3H_2O$	+1.440 V
$4(\ 2Br^- \longrightarrow Br_2 + 2e^-\ )$	-1.087 V
$BrO_4^- + 7Br^- + 8H^+ \longrightarrow 4Br_2 + 4H_2O$	-1.410 V

$\Delta G^o = - nFE^o$

$= - 8x\ 96{,}487\ x\ (-1.410)/4.184$

$= 260.1$ kcal/mol

value of 16.95 l/mol at 25°C. Equilibrium constants at various temperatures are listed in Table 12 for reference. At the beginning, the concentration of bromide can be consider as effectively constant. A constant fraction, Q, of the bromine produced must be present in molecular form. The fraction of molecular bromine is represented as follows:

$$Q = 1/(1 + K[Br^-]),$$

which implies that the formation of tribromide ion is bromide ion concentration dependent, the higher the bromide ion concentration the smaller the fraction of molecular bromine present, or the more tribromide ion formed.

In an analogous oxyhalide reaction, iodate-iodide reaction is ordinarily of the fifth order, but becomes fourth order at very low concentration of iodide [22]. The fourth and fifth order reactions have independent rate-determinig steps [23,24].

The perbromate-bromide fifth order reaction mechanism can be interpreted properly by the facts stated above. That is to say, that the rate law of perbromate-bromide reaction may be a fifth order reaction at high bromide concentration and a fourth order reaction at low bromide concentration. At high bromide concentration, or in the presence of excess bromide, the rate law appears to be fifth order. In this research, the bromide ion was present in excess during all experiments. Therefore, the rate law has been written as the form of equation (2). At low bromide concentration or when an excess of bromide is not present,

TABLE 12

Equilibrium Constants and Standard Gibb's Free Energy of Bromine-Tribromide Distribution

Reaction

$$Br_2 + Br^- \overset{k}{\underset{k'}{\Longleftrightarrow}} Br_3^- \qquad K = k/k'$$

Temperature, °C	ΔG°, cal/mol	K
5	-1650	19.85
25	-1670	16.85
35	-1670	15.28
53.5	-1686	13.42
58	-1689	13.02
63	-1692	12.59
68	-1696	12.20

as described in the experimental section, bromine will be monitored that is to say no significant amount of tribromide will be presented. The rate law was written as the rate of appearance of bromine, d[Br_2]/dt, and shown as a fourth order rate law which is similar to that of periodate-iodide reaction which was confirmed by Abel and Siebenschein [10]. The derivation of the proposed reaction mechanism of perbromate-bromide reaction is presented in Table 13. The rate law derived from this suggested mechanism is found to be consistent with that established by experiments. Bromate-bromide oxidaton-reduction reactions also have been investigated for comparative purposes. The results of the experiments at 308.2 and 328.2K are presented in Table 14. Energy of activation was calculated from two temperatures by the Arrhenius equation, and is presented in Table 15 together with those data from literature [9] as well as for the perbromate-bromide reaction. Activation energies of bromate-bromide, from experiments and literature [9], are consistent. The activation energy for the perbromate-bromide reaction is higher than that of the bromate-bromide reaction by 3.9 kcal/mol.

Table 13

PROPOSED REACTION MECHANISM

$$BrO_4^- + Br^- + 2H^+ \xrightarrow{k1} HBrO_3 + HBrO$$

$$HBrO_3 + Br^- + H^+ \xrightarrow{k2} HBrO_2 + HBrO$$

$$HBrO_2 + Br^- + H^+ \xrightarrow{k3} 2HBrO$$

$$4HBrO + 4Br^- + 4H^+ \xrightarrow{k4} 4Br_2 + 4H_2O$$

$$Br_2 + Br^- \underset{k5'}{\overset{k5}{\rightleftarrows}} Br_3^- \qquad K = k5/k5'$$

$$[HBrO_3] = (k1/k2)[BrO_4^-][H^+]$$

$$[HBrO_2] = (k1/k3)[BrO_4^-]$$

$$[HBrO]^4$$
$$= 3(k1/k4)[BrO_4^-]/[Br^-]^3[H^+]^2$$

$$d[Br_2]/dt = 3(k1)[BrO_4^-][Br^-][H^+]^2$$

$$d[Br_3^-]/dt = (1 - Q)d[Br_2]/dt$$

Since $Q = 1/(1+K[Br^-])$

$$1 - Q = K[Br^-]/(1 + K[Br^-])$$

At the beginning of reaction, the bromide concentration may be considered as constant.

$$d[Br_3^-]/dt$$
$$= 3\{Kk1/(1+K[Br^-])\} \times [BrO_4^-][Br^-]^2[H^+]^2$$

At low bromide concentration, the rate law will be

$$d[Br_2]/dt$$
$$= 3k1[BrO_4^-][Br^-][H^+]^2$$

Table 14

Reaction Rate of the Bromate-Bromide Reaction at I = 0.3, 308.2 K

$10^3[BrO_3^-]$ M	$10^3[Br^-]$ M	$10^8[H^+]$ M	Ratex10^{10}	k
3.33	6.67	0.25	4.92	3.54
3.33	6.67	0.50	19.62	3.53
3.33	6.67	1.00	71.19	3.21
6.66	6.67	0.50	39.01	3.51
9.99	6.67	0.50	64.14	3.85
13.3	6.67	0.50	80.25	3.61

k = 3.54 ± 0.21

Reaction Rate of the Bromate-Bromide Reaction at I = 0.3, 328.2 K

$10^3[BrO_3^-]$ M	$10^3[Br^-]$ M	$10^8[H^+]$ M	Ratex10^{10}	k
3.33	6.67	0.25	17.14	12.35
3.33	6.67	0.50	75.14	13.53
3.33	6.67	1.00	285.43	12.85
3.33	13.34	0.50	117.14	10.58
3.33	20.00	0.50	259.71	15.60
6.66	6.67	0.50	145.43	13.10
9.99	6.67	0.50	190.57	11.44
13.3	6.67	0.50	282.86	12.85

k = 12.78 ± 1.49

* Rate constant k is in the units of $M^{-3}sec^{-1}$

TABLE 15

Comparison of Rate Constants

Temperature C	Bromate-Bromide Experiment k	 Literature k	Perbromate-Bromide Reaction k	 k1
35	3.50	4.02	.	.
40	.	.	.	.
53.5	.	.	900	24.8
55	12.69	12.17	1000	.
58	.	.	1300	37.6
63	.	.	1900	60.9
68	26.84	.	2700	84.2
E, act	12900	12900	16800	18700

Activation energy is in units of cal/mol

V. BIBLIOGRAPHY

(1) E. H. Appelman, Inorganic Chemistry, 90, 1900 (1968).

(2) M. H. Studier, Journal of American Chemical Society, 90, 1901 (1968).

(3) E. H. Appelman, Inorganic Chemistry, 8, 223 (1969).

(4) F. Schreiner, D. W. Osborne, A. V. Pocius and E. H. Appelman, Inorganic Chemistry, 9, 2320 (1970).

(5) E. H. Appelman, U. K. Klaning and R. C. Thompson, Journal of American Chemical Society, 101, 929 (1979).

(6) A. M. Kjaer and J. Ulstrup, Inorganic Chemistry, 21, 3490 (1982).

(7) A. Skrabal and S. R. Weberitsch, Monatsh. 36, 211 (1915).

(8) W. C. Bray and H. A. Liebhafshy, Journal of American Chemical Society, 57, 51 (1935).

(9) J. R. Clark, Journal of Chemical Education, 47, 775 (1970).

(10) E. Abel and R. Siebenschein, Zeitschrift fuer Physicalische Chemie, 130, 631 (1927).

(11) J. N. Bronsted, Zeitshrift fuer Physicalische Chemie, 102, 169 (1922).

(12) N. Bjerrum, Zeitshrift fuer Physicalische Chemie, 108, 82 (1824).

(13) E. H. Appelman, Inorganic Chemistry, 13, 1 (1972).

(14) G. L. Hatch, Thesis, Emporia Teacher State College, (1970).

(15) Graphpac, written by David Kagan, Nov. 1983.

(16) W. F. K. Wynne-Jones and H. Eyring, Journal of Chemical Physics, 3, 492 (1935).

(17) A. G. Sykes, Kinetics of Inorganic Reactions, Pergamon Press, Ltd. Oxford, England, 1966.

(18) P. W. Atkins, Physical Chemistry, W. H. Freeman and Company, San Francisco, 1978.

(19) L. A. Lazarou and T. P. Hadjiioannou, Analytical Chemistry, 51, 790, (1970).

(20) G. K. Johnson, P. N. Smith, E. H. Appleman and W. N. Hubbard, Inorganic Chemistry, 9, 119 (1970).

(21) D. B. Scaife and H. J. V. Tyrell, Journal of Chemical Society, 386 (1958).

(22) Abel and Hifferding, Zeitshrift fuer Physicaliche Chemie, 136, 186 (1982).

(23) Broy, Journal of American Chemical Society, 52, 3582 (1930).

(24) Liebbafsky, Journal of American Chemical Society, 53, 2082 (1931).