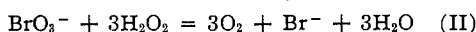


[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

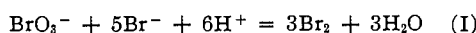
The Kinetic Salt Effect in the Fourth Order Reaction $\text{BrO}_3^- + \text{Br}^- + 2\text{H}^+ \longrightarrow$

BY MARTIN SCLAR AND LEONARD C. RIESCH

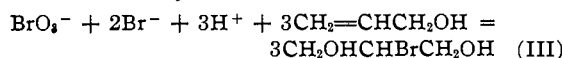
Salt effect in the reaction $\text{BrO}_3^- + \text{Br}^- + 2\text{H}^+ \longrightarrow$ has been investigated by Young and Bray¹ and Bray and Liebhafsky.² The former obtained their results from a study of the reaction



The latter measured initial rates of the reaction



At ionic strengths, μ , above 0.02 the values of the specific velocity constant, k , from reaction I are smaller than those from reaction II, and the difference increases with increasing ionic strength. A kinetic study of the reaction



has now been made, and the results show that this difference remains virtually unchanged when allyl alcohol is used in place of hydrogen peroxide to remove a primary product of the rate controlling reaction.

When equation III is the over-all reaction the differential equation for the rate controlling step, $\text{BrO}_3^- + \text{Br}^- + 2\text{H}^+ \longrightarrow$, is $dx/dt = k(a-x)(b-2x)(c-3x)^2$. a , b and c are the initial concentrations of bromate, bromide and hydrogen ions, respectively, and $a-x$ the concentration of bromate ion at the time t . Integration of this differential equation between the limits 0 and x and 0 and t gives

$$A \log a/a - x + B \log b/b - 2x + Cx/c - 3x + D \log c/c - 3x = kt \quad (\text{IV})$$

$$A = 2.3/(b-2a)(c-3a)^2$$

$$B = 2.3 \times 4/(2a-b)(2c-3b)^2$$

$$C = 9/c(3a-c)(3b-2c)$$

$$D = 2.3 \times 3(4c-3b-6a)/(3a-c)^2(3b-2c)^2$$

Experimental

According to Read and Hurst³ the addition of cold bromine water to an aqueous solution of allyl alcohol results in the formation of $\text{CH}_2\text{OHCHBrCH}_2\text{OH}$ and $\text{CH}_2\text{BrCHBrCH}_2\text{OH}$ due to the addition of hypobromous acid and bromine, respectively; the addition product with hypobromous acid is produced in greater amount. In the experiments reported here advantage was taken of the ease with which allyl alcohol takes

up hypobromous acid. Solutions were prepared whose initial compositions were similar to those used in measuring the rates of reaction III. These solutions were allowed to stand at about 25° until all the bromate ion was consumed; then the residual bromide ion concentrations were determined volumetrically by Volhard's method. The residual hydrogen-ion concentrations were not determined because $\text{CH}_2\text{OHCHBrCH}_2\text{OH}$ is hydrolyzed to glycerol and hydrobromic acid by sodium hydroxide too rapidly to obtain an end-point when titrating. When the initial concentrations of potassium bromate and hydrobromic acid did not exceed 0.0025 and 0.1 M , respectively, the ratio of the change in concentration of bromide ion to that of bromate ion was two. Under these conditions, then, equation III is valid. The ratio, two, was not altered by the addition of the inert salt sodium *p*-toluenesulfonate up to a concentration of 0.79 M ; it was increased by the addition of potassium bromide, which could not, therefore, be used to adjust the ionic strengths of the solutions. Sodium *p*-toluenesulfonate was used for that purpose.

Standardized solutions of potassium bromate, allyl alcohol and inert salt were mixed in an Erlenmeyer flask, and sufficient water was added to make the volume about 110 cc. When the solution acquired the temperature of the thermostat, 10 cc. of hydrobromic acid, also at the temperature of the thermostat, were added from a pipet. The stopper was replaced in the flask, which was then shaken carefully and clamped in the thermostat. From time to time the bromate in 10-cc. portions of the reaction mixture was determined iodimetrically with a sodium thiosulfate solution prepared each day by diluting a carefully standardized 0.015 M stock solution. The consistency of the kinetic data (*cf.* Table I) proves that the analytical method yields accurate results in aqueous allyl alcohol solutions. This might have been predicted from the relative velocities⁴ of the bromate-iodide and bromate-bromide reactions and also from the fact that the iodide was present in excess.

Experiments were carried out at zero and 25°

(1) Young and Bray, *THIS JOURNAL*, **54**, 4284 (1932).

(2) Bray and Liebhafsky, *ibid.*, **57**, 51 (1935).

(3) Read and Hurst, *J. Chem. Soc.*, **121**, 989 (1922).

(4) Skrabal and Weberitsch, *Monatsh.*, **36**, 232 (1915).

between $\mu = 0.021$ and 0.88 and $\mu = 0.051$ and 0.88 , respectively, and at 32.18° at $\mu = 0.097$ and $\mu = 0.51$. When μ exceeded 0.09 the initial concentration of potassium bromate was $0.0025 M$; otherwise it was $0.0012 M$. Sodium *p*-toluene-sulfonate was used only to obtain ionic strengths above 0.1 . The concentration of allyl alcohol was usually $0.014 M$, but a five-fold increase in this concentration did not alter the velocity constant.

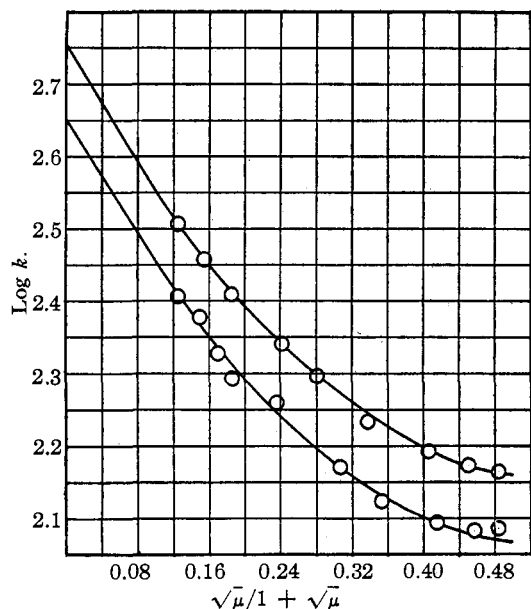


Fig. 1.—Variation of k with ionic strength at 0 and 25° . The 0° curve, which is the lower, is displaced upward 0.8 unit.

The maximum decrease in ionic strength in an experiment could only be 20% ; this decrease could occur when μ was 0.021 , the lowest initial ionic strength used. All but the very slowest reactions were followed until about 85% of the bromate was consumed, and equation IV was found to fit the data well. Each experiment was done in duplicate, and the average difference in the velocity constants of duplicate experiments was 1.0% . Application of equation IV to the bromate-bromide reaction has never been made under conditions unrestricted with respect to changes in the concentrations of reactants. Therefore, it is of interest to present some data showing k is independent of the percentage of bromate consumed. This is done in Table I for an experiment at zero degrees. The detailed 25° and 32.18° results were as consistent as the zero degree results in Table I. In calculating k all concentrations were expressed in moles per liter of solution.

$a =$ Time, min.	$b = c =$ % bromate concns.	$\mu = 0.04162$ initially k
30	6.47	34.7
60	11.95	34.4
90	17.73	33.9
120	22.79	31.4
165	30.05	34.4
226	37.18	33.1
286	44.79	33.8
345	50.82	33.8
1365	91.90	33.5

The results of the experiments at 0 and 25° are presented in Fig. 1, where average values of $\log k$ obtained in two duplicate experiments are plotted against $\sqrt{\mu}/(1 + \sqrt{\mu})$. Kilpatrick⁵ has shown that it might be advantageous to use $\sqrt{\mu}/(1 + \sqrt{\mu})$ rather than $\sqrt{\mu}$ when an extrapolation to zero ion concentration is to be made. From the curves obtained temperature coefficients were calculated at $\mu = 0.0625, 0.0968, 0.290, 0.546$ and 0.819 . They are $7.85, 7.83, 7.88, 7.83$ and 7.74 , respectively, and the average k_{25}/k_0 is 7.84 . This temperature coefficient was used to calculate values of k at 25° at $\mu = 0.02041$ and 0.03365 from the corresponding values on the zero degree curve. The extrapolation to zero ion concentration was made as follows: a line with the theoretical slope required by the Brönsted theory of reaction velocity was moved parallel to itself until it merged smoothly with the curve drawn through the experimentally determined points; this curve was extended somewhat beyond the experimental points in order to make it merge more smoothly

TABLE II
VALUES OF k FOR THE BROMATE-BROMIDE REACTION AT 25°

μ	$k(\text{reaction I})$	$k(\text{reaction II})$	$k(\text{reaction III})$	$k(\text{II})$ is less than $k(\text{III})$ by, %
0	(506)	(540)	(570)	5.3
0.0025	406	(433)	(457)	5.3
.01	337	(360)	(375)	4.0
.04	251	268 ^a	276	2.9
.09	201	219	225	2.7
.16	165	189	194	2.6
.25	141	171	175	2.3
.36	122	159	164	3.0
.49	107	151	156	3.2
.64	93	146	151	3.3
.81	82	142	147	3.4
1.00	71	139	(145)	4.1

^a The data in Ref. 2, Table I, Columns 4 and 7 show that the value 258 given in Column 6 is in error, and should be 268.

(5) Kilpatrick, THIS JOURNAL, **56**, 2326 (1934).

with the line of theoretical slope. The theoretical slopes are $-0.486 \times 4 = -1.94$ and $-0.505 \times 4 = -2.02$, and the straight lines merge with the curves at $\sqrt{\mu}/(1 + \sqrt{\mu}) = 0.10$ and 0.0875 at 0 and 25° , respectively. The equation, $-\log f = 0.5 z^2 \sqrt{\mu}/(1 + \sqrt{\mu})$, is said to be applicable⁵ up to $\mu = 0.03$ or $\sqrt{\mu}/(1 + \sqrt{\mu}) = 0.15$. Values of k at 25° , calculated from the smooth curve in Fig. 1, are listed in Table II together with those obtained from reactions I and II. Numbers in parenthesis were obtained by extrapolation.

The values of k from reaction III are, in general, a little higher than the values of k from reaction II. The agreement, nevertheless, is satisfactory; this is especially so at the higher ionic strengths, where the major portion of the ionic strength was due to different electrolytes. Bray and Liebafsky² concluded that there is little difference in the kinetic salt effects of different electrolytes up to $\mu = 0.4$, and the data now available indicate that this conclusion is valid to $\mu = 1$.

Energies of activation were calculated for three temperature intervals by the Arrhenius equation. They are presented in Table III together with those calculated from the data of Young and Bray¹ for reaction II. The values from reaction II are higher than those from reaction III.

TABLE III
ACTIVATION ENERGY FOR THE BROMATE-BROMIDE REACTION

μ	From Reaction III ^a					
	k (0°)	k (25°)	k (32.18°)	E (25-0°) cal.	E (32.18-25°) cal.	E (32.18-0°) cal.
0.0968	28.1	220	394	13,310	14,670	13,590
.508	19.8	156	257	13,350	12,570	13,190
μ	From Reaction II					
	k (25°)	k (45°)	k (65°)	E (45-25°) cal.	E (65-45°) cal.	E (65-25°) cal.
0.030		1560	8140		17,650	
.055	257 ^b	1335	6730	15,520	17,280	16,340
.105	217	1120	5105	15,460	16,200	15,800

^a Values of k at 0 and 25° taken from Fig. 1.

^b $\mu = 0.0569$.

However, they appear to decrease with decreasing temperature and approach the values from reaction III, which were determined at lower temperatures. With the limited data available further discussion of the decrease in the energy of activation seems unwarranted.

Discussion

Bray and Liebafsky have offered an explanation of the discrepancy in the values of k from reac-

tions I and II. They suggest that the fourth order rate determining reaction is reversible, so that the maximum rate of reaction can be obtained only when a primary reaction product is removed with sufficient rapidity to prevent a reversal of the reaction. Hydrogen peroxide is supposed to react with and remove a primary reaction product more rapidly than does hydrobromic acid.

It is the general opinion of those who have studied the bromate-bromide and similar reactions, that one of the primary reaction products is hypobromous acid. Experiments reported in this article and elsewhere³ show that allyl alcohol takes up hypobromous acid under conditions complied with in the experiments carried out for rate determining purposes. Moreover, this addition reaction is very rapid, because allyl alcohol decolorizes aqueous bromine solutions instantaneously, taking up hypobromous acid as well as bromine. Therefore, it can be concluded that the function of the allyl alcohol in reaction III is to remove the probable primary reaction product, hypobromous acid. The agreement of the specific velocity constants obtained from the two reactions shows that the hydrogen peroxide and allyl alcohol function similarly and with about equal efficiency in reactions II and III, respectively. This is evidence in support of the explanation proposed by Bray and Liebafsky.

We wish to thank the Directors of the Departments of Chemistry and Physiological Chemistry of the University of Pennsylvania for permitting us to use their facilities, and Dr. Martin Kilpatrick for his interest in the work.

Summary

1. Rates of the reaction between bromic and hydrobromic acids in the presence of allyl alcohol were measured at various temperatures and ionic strengths. From the data the energy of activation was calculated, and found to be lower than that obtained by Young and Bray¹ in their study of the reaction in which bromate ion is reduced by hydrogen peroxide.

2. The specific velocity constants obtained at 25° agree with those obtained by Young and Bray. They are higher than those obtained by Bray and Liebafsky,² who measured initial rates of the reaction between bromate and bromide ions in acid solution, and the differences increase with increasing ionic strength.

3. The results support the opinion of Bray

and Liebhafsky, that the fourth order rate determining reaction is reversible, so that the maximum rate of reaction can be obtained only when a primary reaction product is removed with sufficient rapidity to prevent a reversal of the re-

action. Allyl alcohol has been found to be about as efficient as hydrogen peroxide in removing a primary reaction product of the bromate-bromide reaction.

PHILADELPHIA, PA.

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[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY SECTION, PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES]

Vapor Pressures of the Xylenes and Mesitylene¹

BY LOUIS S. KASSEL²

The vapor pressure data given in the "International Critical Tables" for the xylenes, mesitylene, cumene, pseudocumene, *n*-propylbenzene, cymene and isobutylbenzene are based on measurements of Woringer.³ These results give very strongly curved plots of $\log p$ against $1/T$, indicative of serious error, and indeed a few measurements made by Linder⁴ near 0° for several of these compounds showed that Woringer's values at the lower temperatures were much too high. Since it became necessary to calculate entropies of vaporization for the xylenes and mesitylene, the vapor pressures of these substances were re-measured.

Eastman chemicals were used in all cases without further purification other than degassing. The liquid being used was contained in a side tube attached to one arm of a mercury manometer. Both arms were evacuated by a high-speed, mercury diffusion pump until 30–50% of the liquid had evaporated and were then sealed off. The entire manometer system was then immersed in an unsilvered, unevacuated Dewar vessel filled with hot water. Pressures were read with a cathetometer and temperatures with two thermometers calibrated by the Bureau of Standards. With this arrangement it was possible to obtain the vapor pressure curve from 90 to 30° in a few hours. Lower temperatures were obtained by starting with cold water. The accuracy thus attainable is naturally limited, but it is probably as good as the purity of the materials justified. The cathetometer readings were reduced to mm. of a mercury column at 0°.

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(2) Physical chemist, Pittsburgh Experiment Station, U. S. Bureau of Mines, Pittsburgh, Pa.

(3) Woringer, *Z. physik. Chem.*, **34**, 257 (1900).

(4) Linder, *J. Phys. Chem.*, **35**, 351 (1931).

Consideration of all the measurements and data for benzene and toluene led to choice of the equation

$$\log_{10}P = -A/T - 5 \log_{10}T + B$$

The experimental values were fitted by least squares to equations of this type with the following results

$$\begin{aligned} o\text{-xylene } \log_{10}P &= -2830.0/T - 5 \log_{10}T + 22.7480 \\ m\text{-xylene } \log_{10}P &= -2876.3/T - 5 \log_{10}T + 22.9425 \\ p\text{-xylene } \log_{10}P &= -2930.0/T - 5 \log_{10}T + 23.1000 \\ mesitylene \log_{10}P &= -3104.5/T - 5 \log_{10}T + 23.1929 \end{aligned}$$

In these equations 0°C. = 273.2°K. The mean deviation of individual experimental values from the equations is approximately 1% in pressure or 0.2° in temperature for pressures above 10 mm. Table I contains pressures calculated from the equations.

TABLE I

Temp., °C.	VAPOR PRESSURES, MM.			
	<i>o</i> -Xylene	<i>m</i> -Xylene	<i>p</i> -Xylene	Mesitylene
0	1.61	1.71	1.56	0.44
10	3.13	3.35	3.11	.93
20	5.75	6.25	5.90	1.86
30	10.1	11.1	10.7	3.51
40	17.1	19.0	18.4	6.33
50	27.6	31.3	30.7	11.0
60	43.7	49.7	49.3	18.3
70	66.7	76.6	76.7	29.5
80	98.9	114.6	115.9	46.0
90	69.9
100	103.4

Woringer gave 4.0, 1.75, 8.29 and 15.6 mm., respectively, at 0°. These values illustrate the large errors possible in a static method without sufficient degassing. Linder found 1.06, 1.68, 0.95 and 0.375 mm. at 0°. It is difficult to reconcile his low values for *o*- and *p*-xylenes with the present measurements.