

Stoichiometry of Hydrazine-Bromate Reaction in Acid Media

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Abstract Stoichiometry of hydrazine-bromate reaction has been studied in acid media of varying compositions, elucidating the effects of bromide and chloride ions in sulfuric acid, perchloric acid, hydrochloric acid, and hydrobromic acid at varying concentrations of hydrogen ion and cupric ion.

The study shows that the number of red-ox equivalent consumed by one mole of hydrazine becomes practically 4.00 if the concentrations of bromide and hydrogen ions are kept higher than 0.1M and 6M, respectively. The presence of copper tends to reduce the bromate consumption by hydrazine in an irregular manner, but such an effect becomes unimportant if the concentrations of bromide and hydrogen ions are kept sufficiently high.

Introduction

According to Browne and Shetterly¹⁾, a solution of potassium bromate reacts with hydrazine in sulfuric acid, forming appreciable quantities of hydrazoic acid and ammonia, and the amount of the former decreases with increasing acid concentration. Kurtenacker and Wagner²⁾ and Kolthoff³⁾ found that hydrazine can be titrated with potassium bromate solution without suffering from any side reaction when concentrated hydrochloric acid media were used.

Although Hogdkinson⁴⁾ recommends the use

of copper or iron salts as negative catalysts for the side reactions, the present study reveals the contrary; the presence of copper introduces a particular effect. * Furthermore, commercially available hydrochloric acids were found to contain about 2×10^{-5} moles of SO_2 in one liter (ACS specification $10^{-4}\%$); thus, it is expected that the blank consumption of 10^{-3} N KBrO_3 will exceed 0.065ml for every ml of concentrated hydrochloric acid used, and it born out from the present study. Therefore, it is felt desirable to avoid the use of hydrochloric acid in the KBrO_3 titration of hydrazine.

Deshmukh and Bapat⁵⁾ recommended the use of potassium bromide in 4-5 N HCl, and Sant and Mukherji⁶⁾ recommended 0.05M bromide in 2N hydrochloric acid whereas Bishop⁷⁾ recommends 0.1M bromide in 1M hydrochloric acid.

* The initial study on the effect of copper was made when one of the authors(QWC) was working at Prof. Kolthoff's laboratory at Minneapolis. A more detailed account on this problem will be published elsewhere.

Except for those piecewise information, no systematic study of the effect of various ions in bromate-hydrazine titration has been reported in the literature.

The present work deals with variation of the stoichiometry of $\text{BrO}_3^- - \text{N}_2\text{H}_4$ reaction with concentrations of hydrogen, chloride, and bromide ions in the absence and presence of copper ion.

Experimental

Water Doubly distilled water was used throughout the study. The second distillation was made from basic permanganate solution using a Pyrex glass apparatus where the flow of steam was passed through two sharp bents at a linear velocity less than 10 cm/sec. and a three liter flask before reaching the condenser to facilitate trapping of water droplets. The condensate thus obtained contained less than 10^{-9} M/l copper as determined by diethyl-dithio-carbamate method. It was collected in a Pyrex vessel and used within two days, since copper concentration increases to 10^{-7} M/l after storing a week.

Reagents Analytical reagent grade KBr , NaCl , H_2SO_4 , HCl , HClO_4 and HBr were used without further purification. Copper sulfate was dried at 105°C after recrystallization and the monohydrate obtained was converted to the pentahydrate by keeping in a desiccator with moist sodium bromide for a month.

Standard solutions The standard solutions of 0.025M $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$ and 0.1N KBrO_3 were prepared using analytical grade chemicals after recrystallizing from the doubly distilled water more than twice and drying at 150°C and 180°C respectively. The standard solution of hydrazine was stored under nitrogen but not more than ten days.

Nitrogen and oxygen Commercial nitrogen was passed through a heated column of active

copper⁸⁾ to remove traces of oxygen before use. Tank oxygen was used without purification. Both gases were passed through a presaturator containing doubly distilled water to minimize solution evaporation during deaeration.

Apparatus Titrations were carried out using the all Pyrex glass apparatus shown in fig. 1. The essential components are a buret and a titration flask that allow deaeration with desired gas and to keep away from air during titration.

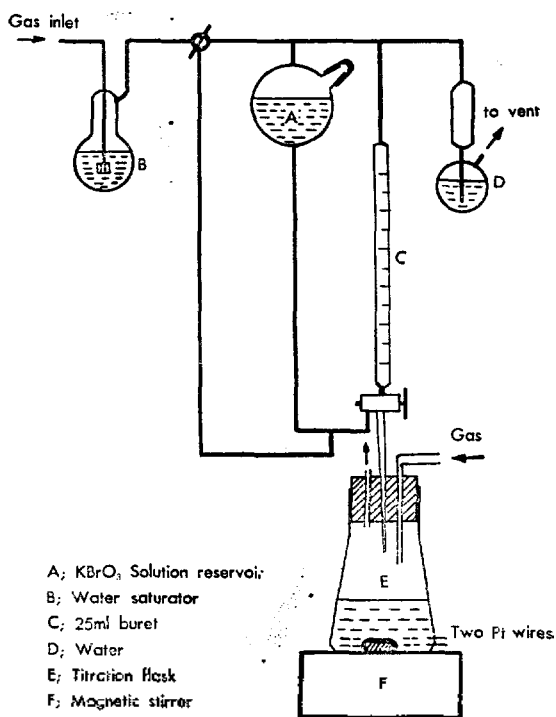


Fig. 1 Schematic diagram of titration apparatus

Procedure All titrations were carried out at room temperature except where otherwise noted. In every titration, appropriate amounts of reagents plus water required to make the entire solution 30 ml were transferred into the titration flask. While deaerating the potassium bromate standard solution in the buret and reservoir, the inside of the titration flask was flushed with a flow of the deaerating gas (oxygen or nitrogen) and the solution was stirred vigorously.

Table 1. Number of equivalents of KBrO_3 consumed by a mole of N_2H_4 in the titration of 0.01 M hydrazine with 0.1 N bromate in H_2SO_4 solutions under N_2 atmosphere at room temperature. (Initial volume of titrand=50ml; contains 0.5m mole of N_2H_4)
Underlined numbers stand for slow titrations.

Br: F	Cu: mM	$[\text{H}^+]_0$ in normal						
		1.64(1.5*)	3	4.5	6	7.5	9	12
0	0	reaction too slow		3.900	3.936	3.982	4.008	4.005
				<u>3.769</u>	<u>3.833</u>	<u>3.950</u>	<u>4.006</u>	<u>4.005</u>
0.05	0	3.863			3.994			
		<u>3.769</u>			<u>3.992</u>			
0.1	0	3.881			3.994			
		<u>3.790</u>			<u>3.996</u>			
0.25	0	3.930			3.998			
		3.872			3.998			
0.5	0	3.960	3.994	4.002	3.999		4.004	
		<u>3.916</u>	<u>3.975</u>	<u>4.000</u>	<u>4.000</u>		<u>4.002</u>	
1.0	0	3.964			4.000			
		<u>3.919</u>			<u>4.002</u>			
0.05	0.073	3.946						
0.1	0.073	3.937						
0.5	0.073	3.860						
1.0	0.073	3.672						
0.05	0.73	3.956	3.921		3.976			
0.1	0.73	3.921	3.915		3.991			
0.25	0.73	3.867	3.879		3.989			
0.5	0.73	3.787	3.859		3.989			
0.75	0.73	3.785	3.855		3.991			
1.0	0.73	3.588	3.897		3.990			
0.05	7.3	3.933						
0.1	7.3	3.925						
0.25	7.3	3.723						
0.5	7.3	3.656						
0.75	7.3	3.494						
0.5	0.01		3.959	3.992	3.997		4.000	
			<u>3.909</u>	<u>3.952</u>	<u>3.993</u>			
0.5	0.1		3.899	3.990	3.909		4.000	
			<u>3.702</u>	<u>3.956</u>	<u>3.979</u>			
0.5	0.73		3.859	3.983	3.989			
			<u>3.637</u>	<u>3.953</u>	<u>3.975</u>			
0.5	2		3.760	3.965	3.990		3.989	
			<u>3.622</u>	<u>3.940</u>	<u>3.975</u>			
0.5	7.3		3.784	3.975	3.991		3.990	
			<u>3.694</u>	<u>3.933</u>	<u>3.975</u>			
0.5	10		3.802		3.990		3.987	
			<u>3.716</u>		<u>3.967</u>			
0.5	30		3.909	3.988	3.989		3.990	
			<u>3.854</u>	<u>3.970</u>	<u>3.979</u>			
0.5	50		3.893					
			<u>3.820</u>					
$[\text{Br}]_0=0$	0	3.795	3.860	3.927	3.980		4.004	
$[\text{Cl}^-]_0=0.5\text{F}$ (NaCl added)		<u>3.630</u>	<u>3.760</u>	<u>3.889</u>	<u>3.962</u>		<u>4.002</u>	

Table 2. Number of equivalents of KBrO_3 consumed by a mole of N_2H_4 in the titration of 0.01 M hydrazine in H_2SO_4 media with 0.1 N bromate under O_2 atmosphere. (Initial volume of titrand=50ml; contains 0.5m mole of N_2H_4)
Underlined numbers stand for slow titrations.

		(a) At room temperature						
[Br ⁻]; F	[Cu ²⁺] _D ; mM	(H ⁺) _e in normal						
		1.64 (1.5*)	3	4.5	6	7.5	9	12
0	0	reaction too slow		3.890	3.918	3.944	3.979	4.001
				<u>3.728</u>	<u>3.793</u>	<u>3.926</u>	<u>3.973</u>	<u>3.999</u>
0.025	0				3.990		3.990	
					<u>3.953</u>		<u>3.985</u>	
0.05	0	too slow			3.992		3.992	
		<u>3.594</u>			<u>3.960</u>		<u>3.988</u>	
0.1	0	<u>3.919</u>			<u>3.987</u>		<u>3.992</u>	
		<u>3.755</u>			<u>3.987</u>		<u>3.992</u>	
0.25	0	<u>3.935</u>					<u>3.996</u>	
		<u>3.821</u>					<u>3.990</u>	
0.5	0	<u>3.963</u>	3.990	3.995	3.995		3.998	
		<u>3.905</u>	<u>3.973</u>	<u>3.993</u>	<u>3.997</u>		3.998	
1.0	0	<u>3.981</u>					3.995	
		<u>3.927</u>					<u>3.995</u>	
0.5	0.01		3.965					
			<u>3.953</u>					
0.5	0.1		<u>3.947</u>					
			<u>3.840</u>					
0.5	0.73		<u>3.892</u>					
			<u>3.686</u>					
0.5	1		<u>3.840</u>					
			<u>3.624</u>					
0.5	2		<u>3.790</u>					
			<u>3.566</u>					
1.0	5		<u>3.744</u>					
			<u>3.518</u>					
(Br ⁻) _e =0 (Cl ⁻) _e in F NaCl added								
0.025	0				3.917			
					<u>3.820</u>			
0.05	0				3.716			
					<u>3.830</u>			
0.10	0				3.922			
					<u>3.894</u>			
0.25	0				3.959			
					<u>3.936</u>			
0.5	0		3.816	3.916	3.975		4.013	
		<u>3.656</u>	<u>3.784</u>	<u>3.876</u>	<u>3.977</u>		<u>4.001</u>	
1.0	0				3.983			
					<u>3.975</u>			
		(b) At 0°C (titration flask immersed in an ice bath)						
0	0			very slow	3.922			
				<u>3.750</u>	<u>3.872</u>			
0.5	0	3.965						
		<u>3.868</u>						
0.5	0.01		3.966					
0.5	0.1		<u>3.910</u>					
0.5	2		<u>3.520</u>					
Br =0	0			3.957				
Cl =0.5F				<u>3.834</u>				
(NaCl added)								

Table 3. Number of equivalents of KBrO_3 consumed by a mole of N_2H_4 in the titration of 0.01M hydrazine in various acid media with 0.1 N bromate at room temperature under N_2 atmosphere. (Initial volume of titrand=50 ml; contains 0.5m mole of N_2H_4)
The result for slow titration is indicated by underlining the numbers. Asterisk designates the experiments under O_2 atmosphere.

$[\text{Br}^-]_0, \text{F}$	$[\text{Cu}^{2+}]_0, \text{mM}$	$[\text{H}^+]_0$ in normality					
		0.5	1.5	3	4.5	6	9(8)
In HCl media							
0	0		3.800 <u>3.719</u>	3.970 <u>3.962</u>	3.992 <u>4.002</u>	4.000 <u>4.000</u>	4.000 <u>4.000</u>
0.5	0	3.970 <u>3.897</u>	4.004 <u>3.976</u>	4.004 <u>3.994</u>	4.002 <u>4.000</u>	4.000 <u>4.001</u>	4.000 <u>4.000</u>
0.5*	0	<u>3.966</u> <u>3.878</u>	3.995 <u>3.953</u>	3.993 <u>3.991</u>	3.993 <u>3.995</u>	3.993 <u>3.993</u>	3.999
0.5	0.01		3.947 <u>3.871</u>	4.004 <u>3.990</u>	3.997 <u>3.995</u>	3.999 <u>3.995</u>	
0.5	0.1		3.848 <u>3.697</u>	3.994 <u>3.968</u>	3.993 <u>3.991</u>	3.999 <u>3.967</u>	
0.5	0.73		3.700 <u>3.404</u>	3.978 <u>3.927</u>	3.991 <u>3.987</u>	3.995 <u>3.977</u>	
0.5	2		3.847 <u>3.636</u>	3.968 <u>3.940</u>	3.989 <u>3.960</u>		
0.5	7.3		3.828 <u>3.750</u>	3.965 <u>3.951</u>	3.975 <u>3.971</u>	3.979 <u>3.957</u>	
0.5	33		3.960 <u>3.939</u>	3.978 <u>3.930</u>	3.975 <u>3.945</u>	3.963 <u>3.939</u>	
In HClO_4 media							
0	0				3.935 <u>3.843</u>	3.969 <u>3.925</u>	4.000 <u>3.990</u> <u>4.004</u>
0.5	0		3.999 <u>3.963</u>	4.003 <u>3.993</u>	4.008 <u>4.008</u>	4.002 <u>4.003</u>	3.999 <u>4.000</u>
0.5*	0		3.976 <u>3.960</u>	3.993 <u>3.989</u>	3.995 <u>3.991</u>	3.995 <u>3.995</u>	3.999 <u>3.997</u>
$[\text{Br}^-]_0=0$ $[\text{Cl}^-]_0=0.5\text{F}$ (NaCl added)	0		3.813 <u>3.682</u>	3.829 <u>3.729</u>	3.908 <u>3.863</u>	3.965 <u>3.939</u>	3.998 <u>3.988</u>
In HBr media							
0.5	0	<u>3.980</u>					
1.5	0		4.001 <u>3.997</u>				
3	0			3.999 <u>4.000</u>			
4.5	0				4.002 <u>4.002</u>		
6	0					4.003 <u>3.998</u>	
0.5*	0	3.977 <u>3.902</u>					
1.5*	0		3.997 <u>3.987</u>				
3*	0			3.999 <u>3.989</u>			
4.5*	0				3.995 <u>3.989</u>		
6*	0					3.998 <u>3.999</u>	

ly for at least fifteen minutes. Then 20 ml of hydrazine standard solution was transferred into the flask. Thus, the initial volume of the titrand was always 50 ml. After slowing down the flow rate of the gas, the three way stopcock was turned in such a way that bubbling through the potassium bromate solution is stopped and gas flows over the solution, and titration was carried out. The end point was determined by biamperometric method with an emf of 0.25 volts applied to the two platinum wire electrodes fused in the titration flask. The titration curve is of reversed-L form⁶⁾.

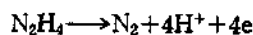
An effort was made to keep the agitation rate constant during titration. Since induced reactions are involved in the titration reaction, an attempt was made to compare the effect of rate of addition of bromate standard solution. Thus, a *slow titration* with dropwise addition of bromate solution at an almost constant interval was carried out first. Normally, it took about 15 minutes. Then, a *fast titration* was carried out by adding bromate solution up to about 95% of the reading of the slow titration as fast as possible then completing by regular titration procedure. It took about 1.5 minutes. The results of the slow titrations are indicated by underlining numbers given in the following tables.

In calculating results, it was assumed that

both the hydrazine sulfate and the potassium bromate used are one hundred per cent pure. The results are expressed in terms of the number of red-ox equivalent consumed by one mole of hydrazine.

Results and Discussion

Table 1, 2, 3, and 4 show results. $[H^+]_0$ designates the initial hydrogen ion concentration computed assuming complete ionization of acids. The general trends of the results are apparent. Since the results tend to 4.00 in most cases, it is certain that the main reaction taking place is



Qualitative observation indicates that the rate of reaction between hydrazine and bromate is the slowest in sulfuric acid media. The presence of chloride or bromide enhances the rate, but bromide has much greater effect.

From the results shown in Table 1 and 2, it can be concluded that, when sulfuric acid or perchloric acid is used, the deviation from the 1 : 4 stoichiometry becomes negligible if bromide concentration greater than 0.1M and hydrogen ion concentration greater than 6M are employed, although the presence of oxygen tends to reduce

Table 4. Number of equivalents of bromate consumed by a mole of hydrazine in the titration of very dilute solutions ($[N_2H_4]_0 = 4 \times 10^{-4}M$) with 0.04 N $KBrO_3$ under N_2 at room temperature. (Initial volume of titrand=50 ml)

	$[Br^-]_0$; F	$[Cu^{2+}]_0$; mM	$[H^+]_0$ in normality				
			1.5	3	4.5	6	8
HCl media	0.5	0	4.009	4.021	4.003	4.001	4.000
			<u>4.013</u>	<u>4.005</u>	<u>3.989</u>	<u>4.000</u>	<u>4.003</u>
H_2SO_4 media	0.5	0	4.028	4.026	4.007	4.007	
			3.997	4.003		4.007	

Since the rate of reaction is rather small, the higher results for fast titrations are likely to be due to overshooting of titration.

bromate consumption slightly. If hydrochloric acid or hydrobromic acid is used, 1 : 4 stoichiometry can be attained at much lower hydrogen ion concentrations.

Table 1, 2, and 3 indicate that the presence of oxygen tends to reduce bromate consumption in an irregular manner. However, such an effect is suppressed appreciably in a medium containing higher concentrations of both bromide and hydrogen ions.

Comparison of (a) and (b) in table 2 indicates that the temperature change from room temperature to 0°C does not seem to have noticeable effects.

Table 4 indicates that 1 : 4 stoichiometry is attained even at lower acidity if very dilute solutions of hydrazine and bromate are used.

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