

## 히드라진과 브롬의 반응의 메카니즘에 관한 연구

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## Study of Hydrazine-Bromine Reaction in Sulfuric Acid Media

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**요 약.** 히드라진과 브롬의 반응속도를 직접 혼합법 및 일정전류 전해법에 의한 브롬화 이온의 전이시간을 측정하는 방법으로 측정하여, 황산 및 브롬화칼륨의 농도가 작을 때에 2차 반응속도 상수는 각각  $10^5$  및  $10^3 \text{ mole}^{-1}\text{sec}^{-1}$ 로 얻어졌다. 이는  $\text{N}_2\text{H}_4 + \text{Br}_2 \rightarrow \text{N}_2\text{H}_2$ ,  $k_1 = 10^5$  및  $\text{N}_2\text{H}_2 + \text{Br}_2 \rightarrow \text{X}$ ,  $k_2 = 10^3$ 인 것으로 간주된다. 황산과 브롬화 이온의 농도가 클 때에는 속도상수가 크게 감소하나 그 원인은 해명하지 못하였다.

**Abstract.** The rate constant for the  $\text{N}_2\text{H}_4$ - $\text{Br}_2$  reaction has been measured in sulfuric acid media by direct mixing method and chronopotentiometric method. The former gave  $10^5 \text{ mole}^{-1} \text{ l sec}^{-1}$  whereas the latter  $10^3 \text{ mole}^{-1}\text{sec}^{-1}$ . It has been inferred that the former represents the rate constant for  $\text{N}_2\text{H}_4 + \text{Br}_2 \rightarrow \text{N}_2\text{H}_2$  and the latter for  $\text{N}_2\text{H}_2 + \text{Br}_2 \rightarrow \text{X}$ .

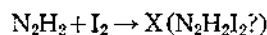
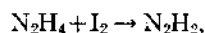
When the concentrations of  $\text{KBr}$  and  $\text{H}_2\text{SO}_4$  are both high, drastic reduction of rate constant has been observed.

### Introduction

It has been shown that the stoichiometry of the reaction of hydrazine and bromate in the presence of bromide in acid media varies depending upon the concentrations of various chemical species<sup>1</sup>. On the other hand, it has been known that the rate determining step of the above mentioned reaction is generation reaction of active oxidizing species,  $\text{Br}_n^{2-n}$ , from bromate<sup>2</sup>.

Nevertheless, there has been no work on

hydrazine-bromine reaction reported yet, although hydrazine-iodine reaction in acid media has been studied<sup>3</sup>. The result of the latter shows that the main reactions are represented by the followings:



$\text{X} \rightarrow \text{N}_2$ . (first order rate constant  $2.6 \times 10^{-3} \text{ sec}^{-1}$  at 25 °C)

A study on the hydrazine-bromate-bromide reaction in acid media indicates that a slowly decomposing intermediate compound, probably

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$N_2H_2Br_2$  is produced by fast reactions between hydrazine and bromine.<sup>2a</sup> In the present work, the direct reaction of hydrazine-bromine has been studied in sulfuric acid solutions. Since a preliminary study revealed the  $N_2H_4-Br_2$  reaction to be extremely fast indeed, it was necessary to study at very low concentrations of hydrazine and bromine. Two methods were used to follow the kinetics of bromine consumption; one was recording the variation of amperometric readings with time and the other was measurement of transition time of constant current electrolysis of  $Br^- + N_2H_4$  solutions at various current densities.<sup>4</sup>

### EXPERIMENTAL

Preparation of stock solution (0.1 M) of hydrazine sulfate has been described<sup>1</sup>. Other reagents (Extra Pure Grade) were used without purification. Nitrogen gas was used after passing through potassium-hydroxide solution of pyrogallol to remove oxygen.

**Apparatus.** In the normal method, an apparatus illustrated in Fig. 1 was fitted with a stopper which holds a platinum indicator electrode, a platinum working electrode with surface area 2 cm<sup>2</sup>, a nitrogen bubbling tube and a K<sub>2</sub>SO<sub>4</sub>

salt bridge from a saturated potassium sulfate-mercurous sulfate reference electrode as shown in Fig. 1. The reference electrode and the indicator electrode were connected to a polarograph (Shimadzu RP-2 Type). With applied voltage 0.26 volts across them, the current readings ( $\sim 1 \mu A$ ) were proportional to the bromine concentration when the solution was stirred by a magnet bar using a magnetic stirrer powered by a Sola constant voltage transformer. A 2 cm<sup>2</sup> platinum electrode was placed in the auxiliary compartment of the reaction vessel separated by a fritted glass membrane from the reaction compartment. The two platinum plate electrodes were connected to a galvanostat (TO-A OM-IA type) and used for generating bromine anodically at constant current in 1~8 mA range. The temperature of the reaction mixture was kept constant at  $20 \pm 1$  °C. In the chronopotentiometry, Varian Electroscam 30 was used.

**Procedure.** A 50 ml portion of solution containing H<sub>2</sub>SO<sub>4</sub> and KBr was added to the reaction compartment of the reaction vessel. The auxiliary compartment of the reaction vessel was filled with the same solution up to the same level as the reaction compartment. Deoxygenated nitrogen was injected for fifteen minutes while the solution was agitated vigorously by using a magnetic stirrer. Then bromine was generated anodically in the reaction compartment of the reaction vessel by a constant current supplied by the galvanostat and the instantaneous concentration of bromine was read amperometrically using the polarograph. A typical recording is duplicated in Fig. 2 by dotted line. After a definite time, the current was turned off and quickly added a measured quantity of hydrazine solution to the reaction compartment; the volume of hydrazine solution used was always less than 1 ml. The amperometric reading was recorded without interruption. The curve CD in Fig. 2 is, in reality, an exten-

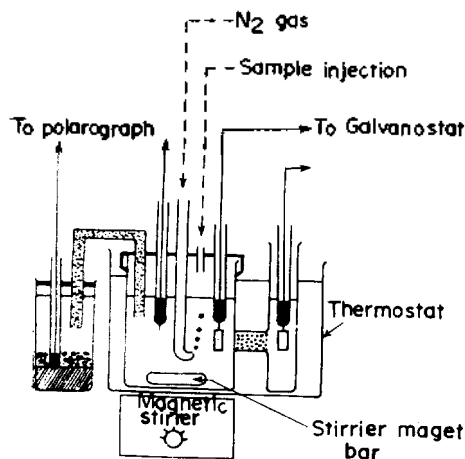


Fig. 1. Cell of kinetic measurements.

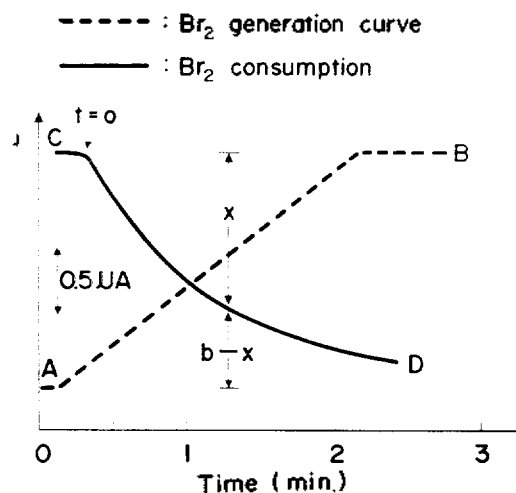


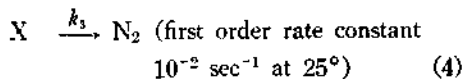
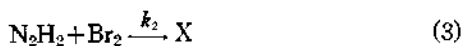
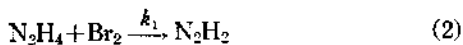
Fig 2. An example of amperometric recording.  
7.2 M H<sub>2</sub>SO<sub>4</sub>, 0.16 M KBr at 20 °C.  
Chart speed 80 mm/min (cf. Table 1).

sion of the curve AB on the recorder chart.

In chronopotentiometry, the cell was filled with appropriate KBr-N<sub>2</sub>H<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> solution and deoxygenated by passing purified nitrogen for fifteen minutes. A platinum plane electrode of 0.23 cm<sup>2</sup> area was used as anode. The transition time was determined graphically from the potential-time trace<sup>5</sup>.

### RESULTS and DISCUSSION

Assuming the main reactions to be represented by



where  $k_1 > k_2 > k_3 = 10^{-2} \text{ sec}^{-1}$  <sup>a2</sup>, the second order rate constant  $k_1$  was calculated from the amperometric readings, according to the integrated form

$$k_1 = \frac{2.30}{(a-b)t} \log \frac{b(a-x)}{a(b-x)} \quad (5)$$

Table 1. Reaction, N<sub>2</sub>H<sub>4</sub>+Br<sub>2</sub>, in water: 7.2 M H<sub>2</sub>SO<sub>4</sub>; 0.16 M KBr at 20 °C.  
 $a = [\text{N}_2\text{H}_4] = 20.1 \times 10^{-5} \text{ M}$ ;  $b = [\text{Br}_2] = 3.37 \times 10^{-3} \text{ M}$

$t$ (sec)	$\frac{2.30}{(a-b)t}$	$x \cdot 10^5$	$(a-x) \cdot 10^5$	$(b-x) \cdot 10^5$	$k_1$
7.5	1840	0.45	19.6	2.91	97
22.5	613	1.16	18.9	2.21	96
37.5	368	1.63	18.4	1.74	92
52.5	263	2.01	18.0	1.36	91
67.5	205	2.28	17.8	1.09	90
82.5	163	2.51	17.5	0.85	88

of the rate equation

$$-\frac{d[\text{Br}_2]}{dt} = k_1[\text{N}_2\text{H}_4][\text{Br}_2] \quad (6)$$

where  $a$  and  $b$  are the initial concentration of hydrazine and bromine, respectively, and  $x$  represents the concentration decrease of bromine. An example is shown in Table 1 which corresponds to the recordings CD of Fig. 2. The calculated value of  $k_1$  decreases gradually, indicating that a slower reaction follows the fast reaction. Therefore, it is plausible that the reaction (2) is much faster than (3) and the rate constant calculated for the initial periods approximately represents the second-order rate constant  $k_1$ . The results obtained at varying concentrations of potassium bromide and sulfuric acid are summarized in Table 2. In Fig. 3 and 4, the results for higher concentration ranges of both potassium bromide and sulfuric acid, where the observed pseudo-second-order rate constant changes drastically, are shown. Table 2 shows that the pseudo-second-order rate constant is almost constant at about  $2 \times 10^5$  when the concentrations of both bromide and sulfuric acid are low. However, the rate constant is inversely proportional to the concentration of sulfuric acid when the latter is very large as shown by Fig. 3. The meaning of the dependence on concentration

Table 2. The effect of concentrations of bromide and sulfuric acid on the second-order rate constant for hydrazine-bromine reaction at 20°C.

KBr M	H <sub>2</sub> SO <sub>4</sub> M					
	1.7×10 <sup>-6</sup>	0.01	0.1	1.0	3.0	
0.3		2.7×10 <sup>5</sup>	2.2×10 <sup>5</sup>	1.5×10 <sup>5</sup>	2.0×10 <sup>5</sup>	
1.0	7.6×10 <sup>4</sup>	2.0×10 <sup>5</sup>	3.0×10 <sup>5</sup>	2.2×10 <sup>5</sup>	6.4×10 <sup>4</sup>	
2.0				9.8×10 <sup>4</sup>	2.1×10 <sup>4</sup>	
3.0		2.3×10 <sup>5</sup>	1.2×10 <sup>5</sup>	5.2×10 <sup>4</sup>	9.3×10 <sup>3</sup>	

KBr M	H <sub>2</sub> SO <sub>4</sub> M						
	3.5	4.0	5.0	6.0	6.2	7.2	8.0
0.85	1.63×10 <sup>5</sup>						
0.1		1.55×10 <sup>4</sup>	1.4×10 <sup>5</sup>	1.1×10 <sup>5</sup>	2.75×10 <sup>5</sup>		
0.16						9.7×10 <sup>1</sup>	
0.3		5.53×10 <sup>4</sup>	7.34×10 <sup>3</sup>	8.65×10 <sup>3</sup>			
0.53							4.87*

\*K<sub>2</sub>SO<sub>4</sub> pptd.

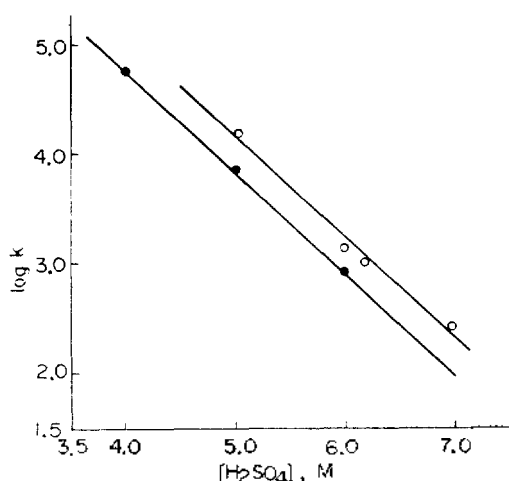


Fig. 3. Effect of sulfuric acid concn. on  $k_{obs}$ .  
○: 0.1 M KBr, ●: 0.3 M KBr.

of bromide and sulfuric acid revealed in Fig. 3 and 4 cannot be explained at the present. A typical result of constant-current electrolysis is represented in Fig. 5 from which the slope of the linear portion was obtained and the pseudo-second-order rate constant was calculated using Eq. (24) of reference (4), assuming  $D_{Br_2} = D_{Br} = 1.0 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ . The rate constants obtained from such procedure are two orders of

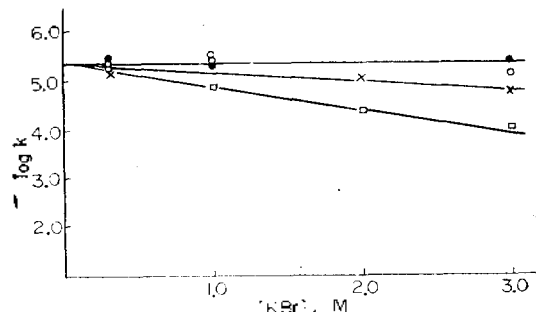


Fig. 4. Effect of bromide concentration on  $k_{obs}$  for hydrazine in various concn. of sulfuric acid.  
●: 0.01 M, ○: 0.1 M, ×: 1.0 M, □: 3.0 M H<sub>2</sub>SO<sub>4</sub>.

magnitude smaller than those obtained in direct mixing method, as shown in Table 3.

If a slower step of bromine consumption follows a fast one, the constant current generation of bromine will give the transition time corresponding to the slower step. Therefore, the smaller rate constant obtained by chronopotentiometric method could be considered as  $k_2$  value for the reaction (2) and the larger value obtained by direct mixing method as  $k_1$  value for reaction (1).

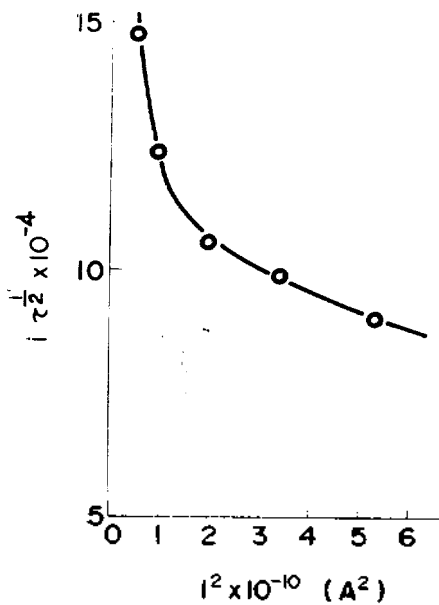


Fig. 5.  $i\tau^{1/2}$  vs.  $i^2$  plot for  $[\text{N}_2\text{H}_4]_0 = 1.0 \times 10^{-3} \text{ M}$ ,  $[\text{Br}^-]_0 = 1.0 \times 10^{-4} \text{ M}$ ,  $[\text{H}_2\text{SO}_4] = 1 \text{ M}$ , at  $21^\circ\text{C}$ .

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Table 3. Pseudo-second-order rate constant of  $\text{N}_2\text{H}_4\text{-Br}_2$  reaction-obtained by chronopotentiometric method at  $21^\circ\text{C}$ .

$[\text{N}_2\text{H}_4]_0 = 1.0 \times 10^{-3}$ ,  $[\text{Br}^-]_0 = 1.0 \times 10^{-4}$ .

Concentration of $\text{H}_2\text{SO}_4$ , M	$k_{\text{obs}}$ , mole <sup>-1</sup> , l, sec <sup>-1</sup> × 10 <sup>-3</sup>
1	1.0
0.01	1.0
0.001	1.2

Uh for technical assistance.

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