Study of Hydrazine-Bromine Reaction in Sulfuric Acid Media

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(Received July 2, 1973)

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

When the concentrations of KBr and H$_2$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 bromine in the presence of bromide in acid media varies depending upon the concentrations of various chemical species$.^1$ 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, Br$^-$. From bromate$^5$.

Nevertheless, there has been no work on hydrazine-bromine reaction reported yet, although hydrazine–iodine reaction in acid media has been studied$.^3$ The result of the latter shows that the main reactions are represented by the followings:

$\text{N}_2\text{H}_4 + \text{I}_2 \rightarrow \text{N}_2\text{H}_2$.
$\text{N}_2\text{H}_2 + \text{I}_2 \rightarrow \text{X} (\text{N}_2\text{H}_2\text{I}_2?)$

$\text{X} \rightarrow \text{N}_2$ (first order rate constant 2.6x10$^{-7}$sec$^{-1}$ at 25°C)

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

Preparation of stock solution (0.1 M) of hydrazine sulfate has been described. Other reagents (Extra Pure Grade) were used without purification. Nitrogen gas was used after passing through potassium-hydroxide solution of pyrogarroll 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 cm², a nitrogen bubbling tube and a K₂SO₄ 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 (~1 μA) 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 cm² 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-1A 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±1 °C. In the chronopotentiometry, Varian Electrosam 30 was used.

Procedure. A 50 ml portion of solution containing H₂SO₄ 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-
RESULTS and DISCUSSION

Assuming the main reactions to be represented by

\[ \text{N}_2\text{H}_4 + \text{Br}_2 \rightarrow \text{N}_2 + \text{Br}_2 \]  
(2)

\[ \text{N}_2\text{H}_4 + \text{Br}_2 \rightarrow \text{X} \]  
(3)

\[ \text{X} \rightarrow \text{N}_2 \text{ (first order rate constant \( 10^{-2} \text{ sec}^{-1} \text{ at } 25^\circ\))} \]  
(4)

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

\[ k_2 = \frac{2.30}{a-b} \log \frac{b(a-x)}{a(b-x)} \]  
(5)

of the rate equation

\[ -\frac{d[\text{Br}_2]}{dt} = k_1[\text{N}_2\text{H}_4][\text{Br}_2] \]  
(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 \( k_2 \). 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

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**Table 1.** Reaction, \( \text{N}_2\text{H}_4 + \text{Br}_2 \), in water: 7.2 \( M \)

\( \text{H}_2\text{SO}_4; 0.16 \text{ M KBr at } 20^\circ\text{C.} \)

\[ a=\{\text{N}_2\text{H}_4\}=2.01 \times 10^{-4} \text{ M}; \ b=\{\text{Br}_2\}=2.37 \times 10^{-4} \text{ M} \]

<table>
<thead>
<tr>
<th>( t ) (sec)</th>
<th>( \frac{2.30}{(a-b)t} )</th>
<th>( x \times 10^3 )</th>
<th>( (a-x) \times 10^4 )</th>
<th>( (b-x) \times 10^6 )</th>
<th>( k_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.5</td>
<td>1840</td>
<td>0.45</td>
<td>19.6</td>
<td>2.91</td>
<td>97</td>
</tr>
<tr>
<td>22.5</td>
<td>613</td>
<td>1.16</td>
<td>18.9</td>
<td>2.21</td>
<td>96</td>
</tr>
<tr>
<td>37.5</td>
<td>358</td>
<td>1.63</td>
<td>18.4</td>
<td>1.74</td>
<td>92</td>
</tr>
<tr>
<td>52.5</td>
<td>263</td>
<td>2.01</td>
<td>18.0</td>
<td>1.36</td>
<td>91</td>
</tr>
<tr>
<td>67.5</td>
<td>295</td>
<td>2.28</td>
<td>17.8</td>
<td>1.09</td>
<td>90</td>
</tr>
<tr>
<td>82.5</td>
<td>163</td>
<td>2.51</td>
<td>17.5</td>
<td>0.85</td>
<td>88</td>
</tr>
</tbody>
</table>

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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.

<table>
<thead>
<tr>
<th>KBr M</th>
<th>H₂SO₄ M</th>
<th>KBr M</th>
<th>H₂SO₄ M</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.01</td>
<td>0.1</td>
<td>1.0</td>
</tr>
<tr>
<td>0.3</td>
<td>1.7×10⁻⁴</td>
<td>2.7×10⁻⁴</td>
<td>2.0×10⁻⁴</td>
</tr>
<tr>
<td>1.0</td>
<td>7.6×10⁻⁴</td>
<td>2.0×10⁻¹</td>
<td>3.0×10⁻⁴</td>
</tr>
<tr>
<td>2.0</td>
<td></td>
<td>9.8×10⁻⁴</td>
<td>2.0×10⁻⁴</td>
</tr>
<tr>
<td>3.0</td>
<td>2.7×10⁻⁴</td>
<td>1.2×10⁻⁶</td>
<td>5.0×10⁻⁴</td>
</tr>
</tbody>
</table>

*K₂SO₄, pptd.

Fig. 3. Effect of sulfuric acid concn. on k₂ₐ₉. ○: 0.1 M KBr. ●: 0.3 KBr.

Fig. 4. Effect of bromide concentration on k₂ₐ₉, for hydrazine in various concn. of sulfuric acid. ○: 0.01 M, ○: 0.1 M, ○: 1.0 M, □: 3.0 M H₂SO₄.

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 k₂ value for the reaction (2) and the larger value obtained by direct mixing method as k₁ value for reaction (1).

Journal of the Korean Chemical Society
Fig. 5. $i_{\frac{1}{2}}$ vs. $i^2$ plot for $(N_2H_4)_2=1.0 \times 10^{-4} M$, $[Br^-]=1.0 \times 10^{-4} M$, $(H_2SO_4)=1 M$, at 21°C.

ACKNOWLEDGEMENT

The authors are grateful to Ministry of Education for partial support of the present work. They also thank Mr. Y. K. Kong and Mr. Y. S. Uh for technical assistance.

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