

# Kinetics and Mechanism of $N_2H_4$ - $KBrO_3$ Reaction in the Presence of Allyl Alcohol<sup>†</sup>

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Kinetics and Mechanism of  $N_2H_4$ - $KBrO_3$  reaction in the presence of allyl alcohol have been studied. The pseudo-first order rate constant for gas evolution was found to be  $10^{-4}$ ~ $10^{-3}$  sec<sup>-1</sup> at  $25.0 \pm 0.1^\circ C$ , increasing with concentration of hydrogen ion. When concentrations of sulfuric acid and allyl alcohol are both sufficiently high, the following overall reaction explains experimental results reasonably well:  $N_2H_4 + BrO_3^- + H^+ \rightarrow N_2 + HOBr + 2H_2O$ ,  $CH_2 = CHCH_2OH + HOBr \rightarrow CH_2 - OHCHBrCH_2OH$ . More complicated reaction mechanisms at lower acidity conditions have been contemplated.

## Introduction

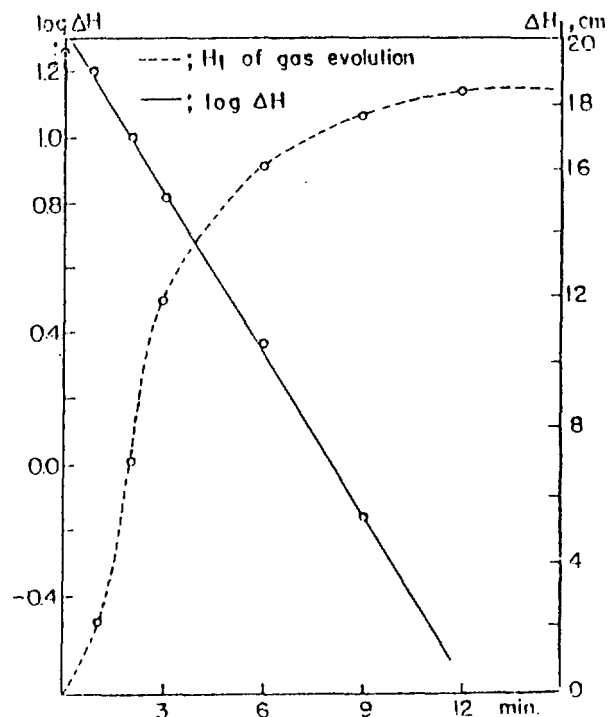
It is well known that the reaction of bromate ion with hydrazine in acidic media in the presence of bromide ion is one of the Landolt reaction; namely, the overall reaction rate is determined by the rate of formation of bromine, for which bromide ion is a necessary reactant. No attempt has been made to elucidate the contribution of bromate ion itself in the  $N_2H_4$ - $KBrO_3$  reaction so far.

The present study deals with the direct reaction of hydrazine and bromate ion in the absence of bromide ion. In order to assure the absence of bromide ion, scavenging action of allyl alcohol is utilized.

## Experimental

**Reagents.** The preparation of doubly distilled water, hydrazine sulfate, potassium bromate, potassium iodate, bromine and oxygen-free nitrogen have been described previously.<sup>1,2</sup> All other reagents were analytical reagent grade and used without further purification. Bromide-free HOBr was prepared from  $Br_2$  and  $Ag_2SO_4$  according to Chapin<sup>3</sup> and Betts.<sup>4</sup>

**Apparatus.** All reactions for kinetic study were carried out in a closed reaction vessel with an opening fitted with a septum membrane stopper for injecting chemicals, and the reaction vessel was connected to a manometer to follow gas generation in thermostat bath ( $25.0 \pm 0.1^\circ C$ ). The hydrazoic acid in the reaction mixture was determined by distilling into an acidified ferric nitrate solution and measuring absorbance at 460 nm.<sup>5</sup> Ammonia was determined by specific ion meter (Orion Model 407A) and ammonia electrode (Orion Model 95-10). Also, bromide ion was determined by specific ion meter (Electrochemical Instrumental Model HGC-10) and bromide electrode (Electrochemical Instrumental Model 7040-IP). Propyl alcohol produced by the diimide-allyl alcohol reaction was determined by using a GC (Yanaco G180) equipped with a col-



**Figure 1.** Typical kinetic data showing the determination of pseudo-first order rate constant for gas evolution in  $N_2H_4$ - $KBrO_3$  reaction in the presence of  $CH_2 = CHCH_2OH$  at  $25.0 \pm 0.1^\circ C$ .

$[N_2H_4]_0 = 10.00 \times 10^{-3} M$ ;  $[KBrO_3]_0 = 1.000 \times 10^{-3} M$ ;  
 $[CH_2 = CHCH_2OH]_0 = 9.0 \times 10^{-3} M$ ;  $[H_2SO_4]_0 = 2.0 M$ .

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**Procedures.** In the kinetic measurements, the solution containing all components except for potassium bromate was transferred to the reaction vessel and saturated with purified nitrogen gas while the solution was stirred vigorously with a magnetic stirrer. Then the potassium bromate solution saturated with the same gas was introduced at an appropriate speed. In the kinetic measurements, an effort was made to stir the solution vigorously enough to attain gas-solution

<sup>†</sup> Based on the thesis of K.H. Chung submitted to Seoul National University in 1983 in partial fulfillment of requirements for a Ph.D.

Table 1. Stoichiometry of  $N_2H_4$ - $BrO_3^-$  Reaction in sulfuric Acid Media:  $[N_2H_4]_0 = 10.00 \times 10^{-3} M$  (1.50 mmoles);  $[KBrO_3]_0 = 1.000 \times 10^{-3} M$  (0.150 mmoles) at  $25.0 \pm 0.1^\circ C$

$[H_2SO_4]_0, M$	$K \times 10^3$ $sec^{-1}$	$\Delta H, cm$ (26.45*)	converted $\Delta H$ to the No. of moles of $N_2 \times 10^3$ (A)	converted $HN_3$ to the No. of moles of $N_2$ , $\times 10^3$ (B); (No. of moles of $HN_3$ )	converted $NH_3$ to the No. of moles of $N_2$ , $\times 10^3$ (C); (No. of moles of $NH_3$ )	Total No. of moles of $N_2$ , (A+B+C), $\times 10^3$ (22.50*)	No. of moles of $Br^-$ , $\times 10^3$ (0.150*)
0.50	0.57	18.46	15.70	5.16 (3.44)	1.72 (3.45)	22.58	0.145
1.0	2.18	18.37	15.63	5.08 (3.39)	1.69 (3.38)	22.40	0.148
2.0	14.75	21.68	18.44	3.18 (2.12)	1.06 (2.11)	22.68	0.149
3.0	20.65	23.97	20.39	2.07 (1.38)	0.68 (1.37)	23.14	0.150
5.0	22.93	26.32	22.39	0.18 (0.12)	0.11 (0.22)	22.68	0.150

\* Theoretical value.

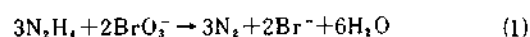
Table 2. Stoichiometry of  $N_2H_4$ - $BrO_3^-$  Reaction in Sulfuric Acid Media in the presence of allyl alcohol:  $[N_2H_4]_0 = 10.00 \times 10^{-3} M$  (1.50 mmoles);  $[KBrO_3]_0 = 1.000 \times 10^{-3} M$  (0.150 mmoles) at  $25.0 \pm 0.1^\circ C$

$[H_2SO_4]_0, M$	$[CH_2CHCH_2OH]_0$ $\times 10^3 M$	$K \times 10^3$ $sec^{-1}$	$\Delta H, cm$ (26.45*)	converted $\Delta H$ to the No. of moles of $N_2 \times 10^3$ (A)	converted $HN_3$ to the No. of moles of $N_2 \times 10^3$ (B); (No. of moles of $HN_3$ )	converted $NH_3$ to the No. of moles of $N_2 \times 10^3$ (C); (No. of moles of $NH_3$ )	Total No. of moles of $N_2$ , (A+B+C), $\times 10^3$ (22.50*)	No. of moles of $Br^-$ , $\times 10^3$ (0.150*)
0.50	1.5	0.26	21.11	17.96	4.29(2.86)	1.27(2.53)	23.52	0.145
	6.0	0.24	21.47	18.27	2.43(1.62)	0.76(1.51)	21.46	0.139
	9.0	0.23	21.45	18.24	1.83(1.22)	0.46(0.91)	20.53	0.130
1.0	20.0	0.16	27.71	23.57	0.32(0.21)	0.12(0.24)	24.01	0.114
	1.5	1.78	20.27	17.24	3.92(2.61)	1.34(2.67)	22.50	0.138
	6.0	1.60	20.41	17.36	3.62(2.41)	1.34(2.67)	22.32	0.126
2.0	9.0	1.30	22.19	18.88	1.98(1.32)	0.66(1.32)	21.52	0.117
	20.0	1.27	23.65	20.12	1.43(0.95)	0.56(1.11)	22.11	0.089
	1.5	13.40	19.46	16.55	4.05(2.70)	1.78(2.56)	22.38	0.138
3.0	6.0	7.89	17.59	14.96	3.08(2.05)	0.81(1.61)	18.85	0.103
	9.0	6.25	17.72	15.07	2.78(1.85)	0.87(1.74)	18.72	0.083
	20.0	5.25	18.56	15.79	1.62(1.08)	0.67(1.33)	18.08	0.043
5.0	1.5	19.39	21.68	18.44	1.79(1.19)	0.59(1.17)	20.82	0.140
	6.0	8.30	18.09	15.38	1.74(1.16)	0.58(1.15)	17.70	0.063
	9.0	7.15	16.61	14.13	1.71(1.14)	0.62(1.24)	16.46	0.035
5.0	20.0	6.42	13.96	11.87	1.38(0.92)	0.48(0.95)	13.73	0.009
	1.5	20.30	24.11	20.50	0.24(0.16)	0.07(0.14)	20.82	0.132
	6.0	17.36	18.90	16.08	0.18(0.12)	0.07(0.13)	16.33	0.018
	9.0	13.82	9.25	7.87	0.12(0.08)	0.06(0.11)	8.05	0.001
	20.0	10.14	8.17	6.95	nd	0.02(0.03)	6.97	0.001

\* Theoretical value.

equilibrium as fast as possible. The pressure increase ( $\Delta H$ ) observed due to the reaction was read with a barometer. The pseudo-first order rate constant for gas evolution in the  $N_2H_4$ - $BrO_3^-$  reaction in the presence of allyl alcohol under various conditions was evaluated by plotting  $\log \Delta H$  vs. time as shown in Figure 1.

The theoretical value of the pressure change was computed by assuming the overall reaction (1) and the gas phase to behave as an ideal gas.

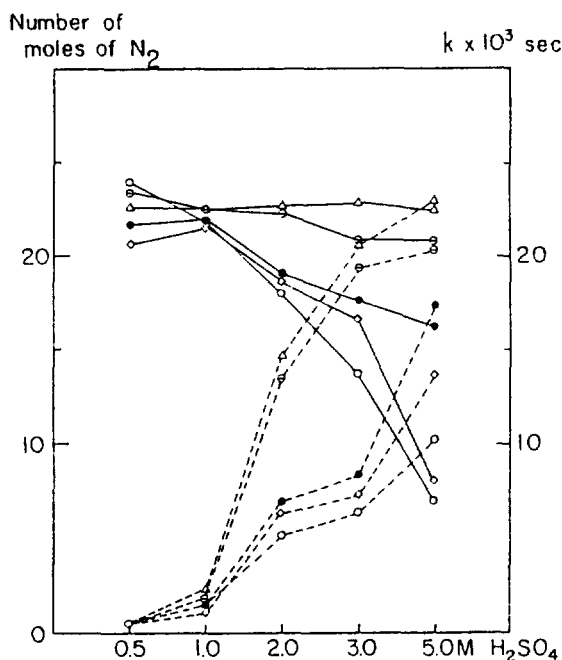


## Results

**Stoichiometry of hydrazine-bromate reaction in the absence of allyl alcohol.** The experimental results are summarized in Table 1. The pseudo-first order constant for gas evolution was found to be  $5.7 \times 10^{-4} \sim 2.3 \times 10^{-2} sec^{-1}$  at  $25.0 \pm 0.1^\circ C$ , increasing with concentration of hydrogen ion. The order of magnitude of the gas evolution rate constant agrees with that observed in the  $N_2H_4$ - $Br_2$  reaction<sup>1</sup> when the hydrogen ion concentration is sufficiently high. However, it is much smaller than the latter at lower hydrogen ion concentration, suggesting that gas evolution reaction is controlled by

**Table 3. Number of Moles of Hypobromous Acid Consumed Hydrazine at Various Concentrations of Sulfuric Acid under Room Temperature;  $[N_2H_4]_0 = 4.0 \times 10^{-3} M$**

$[H_2SO_4]_0, M$	0.02	0.04	0.50	1.00	2.00
stoichiometric ratio	2.00	1.99	2.01	2.02	1.97



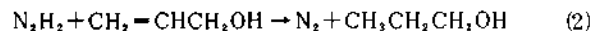
**Figure 2.** Dependence of pseudo-first order rate constants for gas evolution on sulfuric acid concentration (dotted line) and total number of moles of  $N_2$  detected in  $N_2H_4$ - $KBrO_3$  reaction (solid line) in the presence of  $CH_2=CHCH_2OH$  at  $25.0 \pm 0.1^\circ C$ .  $[N_2H_4]_0 = 10.00 \times 10^{-3} M$  (1.50 mmol);  $[KBrO_3]_0 = 1.000 \times 10^{-3} M$  (0.15 mmol).  $\Delta$ , no  $CH_2=CHCH_2OH$ ;  $\circ$ ,  $1.5 \times 10^{-3} M$   $CH_2=CHCH_2OH$ ;  $\bullet$ ,  $6.0 \times 10^{-3} M$   $CH_2=CHCH_2OH$ ;  $\diamond$ ,  $9.0 \times 10^{-3} M$   $CH_2=CHCH_2OH$ ;  $\circ$ ,  $2.0 \times 10^{-2} M$   $CH_2=CHCH_2OH$ .

the rate of precursor formation of gas forming reaction. Total number of moles of nitrogen (A + B + C) produced by reaction (1) is 103% to 99.6% of theoretical value ( $22.50 \times 10^{-5}$  moles). The number of moles of hydrazoic acid and ammonia produced in the  $N_2H_4$ - $KBrO_3$  reaction are almost equal except for higher concentration of  $H_2SO_4$ , such as 5.0 M; the number of moles of bromide ion produced by the reaction is 100% to 97.0% of that of the bromate consumed ( $15.0 \times 10^{-5}$  moles) independent of  $H_2SO_4$  concentration.

**Stoichiometry of hydrazine-bromate reaction in the presence of allyl alcohol.** The experimental results are summarized in Table 2. The pseudo-first order rate constant for gas evolution was found to be  $1.6 \times 10^{-4} \sim 2.0 \times 10^{-2} \text{ sec}^{-1}$  at  $25.0 \pm 0.1^\circ C$ , increasing with concentration of hydrogen ion, which is quite different from the case where allyl alcohol was absent. Total number of moles of nitrogen (A + B + C) produced is 97.0% to 0.67% of that of the bromate consumed ( $15.0 \times 10^{-5}$  moles). Dependence of pseudo-first order rate constant for gas evolution and total number of moles of nitrogen produced by

reaction is shown in Figure 2.

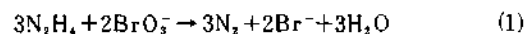
$CH_2CH_2CH_2OH$  produced due to reaction (2)<sup>6,7</sup> was determined by gas chromatographic method and was  $5.09 \times 10^{-5}$  moles under  $20.0 \times 10^{-3} M$   $CH_2=CHCH_2OH$ ,  $0.5 M$   $H_2SO_4$ ,  $10.00 \times 10^{-3} M$   $N_2H_4$ , and  $1.000 \times 10^{-3} M$   $KBrO_3$  condition.



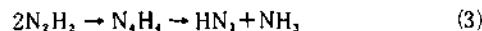
The result of the stoichiometry of the  $N_2H_4$ - $HOBr$  reaction was found to be the moles ratio of 1:2 (in  $0.01 \sim 2.00 M$   $H_2SO_4$ ) as shown in Table 3.

## Discussion

In Table 1, the ratio  $\Delta[HN_3]/\Delta[NH_3]$  was found to be unity, suggesting that contribution of one electron oxidation; e.g.,  $BrO_2$  formation<sup>8,9</sup> has negligible effect. In Table 2, except for  $H_2SO_4 = 3.0 M$  (in  $20.0 mM$   $CH_2=CHCH_2OH$ ) and  $H_2SO_4 = 5.0 M$  (in  $9.0 \sim 20.0 mM$   $CH_2=CHCH_2OH$ ), total number of moles of nitrogen produced by reaction is equal to the number of moles of potassium bromate plus the half of the number of moles of bromide ion produced by reaction. Namely, the overall reaction can be represented by



Furthermore, When  $[H_2SO_4]$  is lower than 3.0M, up to 9.0mM allyl alcohol, bromate-allyl alcohol reaction is sufficiently slow compared with bromate-hydrazine reaction. When  $H_2SO_4 = 5.0M$ , the effect of the presence of  $CH_2=CHCH_2OH$  is most prominent: as  $[CH_2=CHCH_2OH]$  increases, the formation of  $Br^-$ ,  $HN_3$ , and  $NH_3$  all tends to be negligible. The ratio of  $[N_2]$  to  $(3[HN_3] + [NH_3])/2$  approaches 4:1 when, up to  $H_2SO_4 = 2.0M$ ,  $CH_2=CHCH_2OH = 1.5mM$ . From the results shown in Table 2, it is certain that diimide is the intermediate product of the reaction between hydrazine and bromate ion. When hydrogen ion concentration is not large, dimerization reaction (3)<sup>10</sup> and hydrogenation reaction of diimide (2) are not disturbed severely by protonation.

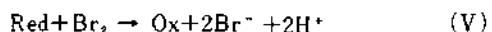
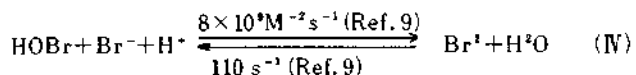
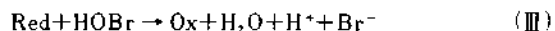
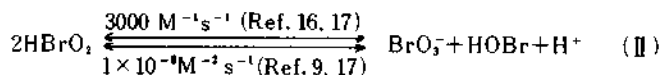
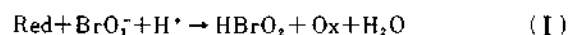


Thus at lower hydrogen ion concentrations, more  $HN_3$  and  $NH_3$  are produced when allyl alcohol concentration is lower. Allyl alcohol reacts rapidly with hypobromous acid through addition at double bond.<sup>11</sup> Although it has been reported<sup>8</sup> that allyl alcohol reacts negligibly slowly with bromate compared with hypobromous acid, we found that, in 5M  $H_2SO_4$  solution containing  $9.0 \sim 20.0 mM$   $CH_2=CHCH_2OH$ , it reacts fairly rapidly with  $BrO_3^-$ ;  $CH_2=CHCH_2OH$  consumes about a half of  $BrO_3^-$  in the time required for completion of the  $N_2H_4$ - $BrO_3^-$  reaction when  $[N_2H_4] = 10.00 \times 10^{-3} M$  and  $[BrO_3^-] = 1.000 \times 10^{-3} M$ .

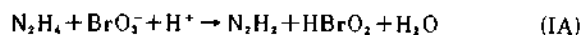
The stoichiometry of the  $N_2H_4$ - $HOBr$  reaction in sulfuric acid solution is found to be 1:2 as shown in Table 3. The reaction of hydrazine with hypobromous acid is extremely fast; under the conditions given in Table 3, nitrogen evolution starts immediately on mixing. Hypobromous acid is a strong enough two equivalent oxidant.<sup>8, 12-14</sup> In the reaction of hydrazine with the conventional two-electron oxidants ( $BrO_3^-$ ,  $IO_3^-$ , etc.),

hydrazine is converted to  $N_2$  by a pair of 2e transactions.<sup>15</sup>

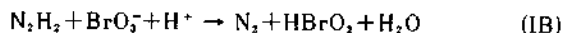
The reduction of bromate ion in acidic media can be described by a certain combination of the following reaction:



In the present work,  $N_2H_4$  and  $N_2H_2$  both can be treated as Red in the above scheme. Thus, the initiation of the entire series of reaction is the reduction of bromate ion by hydrazine according to the reaction (IA).

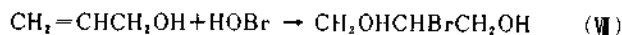
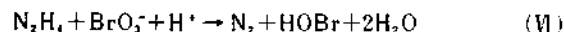


The bromous acid disproportionates to form hypobromous acid and bromate ion according to the reaction (II) as soon as it forms. Therefore, the rest of the reaction is determined by the fate of hypobromous acid. When acidity is high, the scavenging action of allyl alcohol can compete with the reaction of hydrazine and/or diimide and hypobromous acid (III). According to Table 2, at sufficiently high concentrations of both allyl alcohol and sulfuric acid, no bromide ion is produced, indicating that neither (III) nor (V) can participate, which means that allyl alcohol scavenges hypobromous acid as soon as it forms. Under such conditions, the amount of hydrazine consumed by bromate is not represented by the reaction(I); instead, the prevailing reactions for the consumption of hydrazine are the reactions (IA), (II), and (IB),



in addition to the allyl alcohol -  $\text{BrO}_2$  reaction. Thus, when hydrogen ion concentration is high, the overall reaction can be represented by (IA) + (II) + (IB) or (VI), in addition to (VII).

If the reaction is presented by (I), the ratio of the number of nitrogen formed to the number of moles of bromate consumed is 3/2:1. However, if the reaction mechanism is (IA) + (II) + (IB), it will be equal to 1:1. Furthermore, if allyl



alcohol also reacts with bromate ion, it will be reduced further. Keeping these in mind, Figure 2 can be interpreted with the above mentioned proposals.

However, as the concentration of hydrogen ion is lowered, the scavenging reaction (VII) becomes slower than the reactions of hypobromous acid with hydrazine and its derivatives so that the latter gradually dominates; the reaction (IB) is almost completely suppressed and diimide is consumed by the reaction(III). The product of the latter reaction will end up with the formation of  $N_2$  and  $\text{Br}^-$ .

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