

황산 산성용액에서의 $N_2H_4-I_2$ 반응의 속도론적 연구

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(1975. 3. 6 접수)

Kinetics of $N_2H_4-I_2$ Reaction in Sulfuric Acid Media

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(Received March 6, 1975)

요 약. 요오드와 히드라진 사이의 반응을 요오드의 소비속도와 기체발생 속도를 비교하는 방법으로 검토하였다. 낮은 pH에서는 요오드의 소비속도가 율속단계이나 중성 및 약한 산성에서는 기체발생 속도가 율속과정이다. 요오드 소비속도가 기체 발생속도의 1000 배쯤 된다. 이들 사실을 설명하기 위하여 중간물(아마 $N_2H_2I_2$)이 생성되어 그 분해속도 상수가 중성에서 약 $1.5 \times 10^{-3} \text{ sec}^{-1}$ 쯤 된다는 가정을 제시하였다.

ABSTRACT. The rates of consumption of iodine and gas evolution in hydrazine-iodine reaction in the presence of large excess of hydrazine have been studied in the pH range 0.5~7. They are the same at very low pH and both increase to respective asymptotic values as pH is increased. The rate of iodine consumption is three orders of magnitude faster than the rate of gas evolution at higher pH. The results are explained by postulating that N_2H_4 but not protonated form reacts with iodine and an intermediate, probably $N_2H_2I_2$, is formed which decomposed by first order reaction of rate constant about $1.5 \times 10^{-3} \text{ sec}^{-1}$ in neutral and weakly acidic solutions.

INTRODUCTION

It has been reported that the rate of gas evolution in $N_2H_4-I_2$ reaction is almost the same as that of iodine consumption in the pH range 1~1.5, although the pH dependence is rather complicated¹. The purpose of the present work is to clarify the effect of hydrogen-ion concentration on the above mentioned reaction. The rates of both gas evolution and iodine consumption have been studied in a wide range of hydrogen-ion

concentration (pH=0.5~7).

EXPERIMENTALS

The apparatus used in the study of gas evolution and the reagents used are the same as those described in the previous report¹. In addition, dilute solutions of sodium hydroxide prepared by using reagent grade chemicals are used in neutralizations. A pH meter (Fisher Model) is used for pH measurement. Since the amount of hydrogen ion produced by $N_2H_4-I_2$ reaction is expected to

be always smaller than either sulfuric acid or hydrazine present in the solution, their buffer action should keep the pH of reaction mixture almost constant while the reaction proceeds.

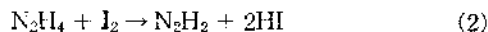
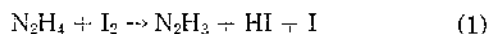
The reaction vessel for the study of iodine consumption is a 250 ml Erlenmeyer flask fitted with a four hole rubber stopper, two for inlet and outlet of sweeping gas (nitrogen), and two for platinum electrodes of 1 mm diameter and 2 cm long. The electrodes are connected to a voltage source and current recording circuit as shown in Fig. 1. An X-Y recorder (815M Plotmatic, MFE Corp. U. S. A.) is used. When the solution is stirred at a constant rate, the current flowing through the two polarized electrodes will be proportional to the analytical concentration of iodine. When a large excess of iodine is used, a bucking circuit is used to subtract the large constant current that is expected at the end of the reaction, as shown in (B). Such a scheme makes it possible to expand the span of the current change due to the iodine consumption to almost the full scale range.

Since the rate of iodine consumption in higher pH region is very large, iodine is added to the

reaction vessel containing all other reagents by using a hyperdermic syringe. Other than that, the procedure is the same as described previously.

RESULTS and DISCUSSION

Typical recordings and the corresponding first order rate plot, $\log(i-i_\infty)$ vs. t , are shown in Fig. 2. It is clear that the iodine consumption follows a first order kinetics, indicating that the slowest step of iodine consumption in the possible reactions given below is a first order reaction.



In strongly acidic solutions, both the rates of gas evolution and iodine consumption are first order in hydrazine concentration as shown in Fig. 3. However, the reaction rate of iodine consumption is independent of iodine concentration at lower pH as shown in Fig. 4. The variation of the pseudo-first order rate constants measured at a iodine concentration, where the rate of iodine consumption is independent of its concentration,

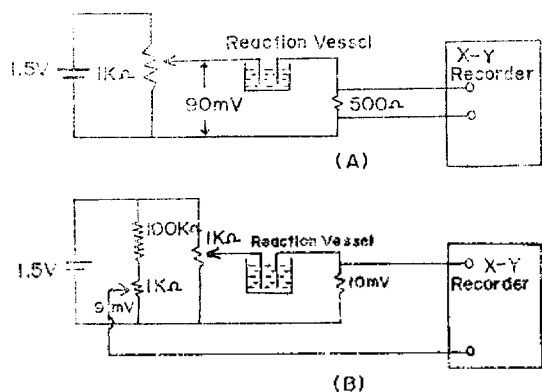


Fig. 1. Diagrams of current recording circuit used to follow the variation of iodine concentration by biampometric method.

A: for small concentration of iodine.

B: for large concentration of iodine.

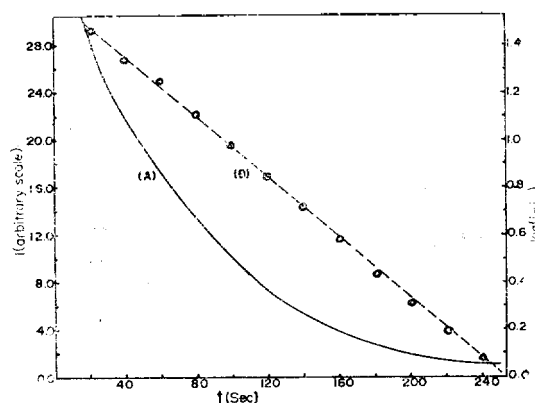


Fig. 2. Typical recording of biampometric current (A) and its $\log(i-i_\infty)$ vs. time plot (B). $(\text{N}_2\text{H}_4)_0 = 3 \times 10^{-2} \text{ M}$; $(\text{I}_2)_0 = 0.97 \times 10^{-3} \text{ M}$; $(\text{KI})_0 = 5 \times 10^{-3} \text{ M}$; $[\text{H}^+] = 0.15 \text{ M}$.

is shown in Fig. 4. As the pH of the solution increases, both the rates of gas evolution and iodine consumption increases to respective asymptotic values. The fraction of singly protonated hydrazine varies with hydrogen concentration according to

$$\alpha_1 = \frac{[N_2H_5^+]}{C_{N_2H_4}} = \frac{[N_2H_5^+]}{[N_2H_4] + [N_2H_5^+] + [N_2H_6^{2+}]} = \frac{K_1[H^+]}{K_1K_2 + K_2[H^+] + [H^+]^2} \quad (6)$$

Where $C_{N_2H_4}$ = analytical concentration of hydrazine,

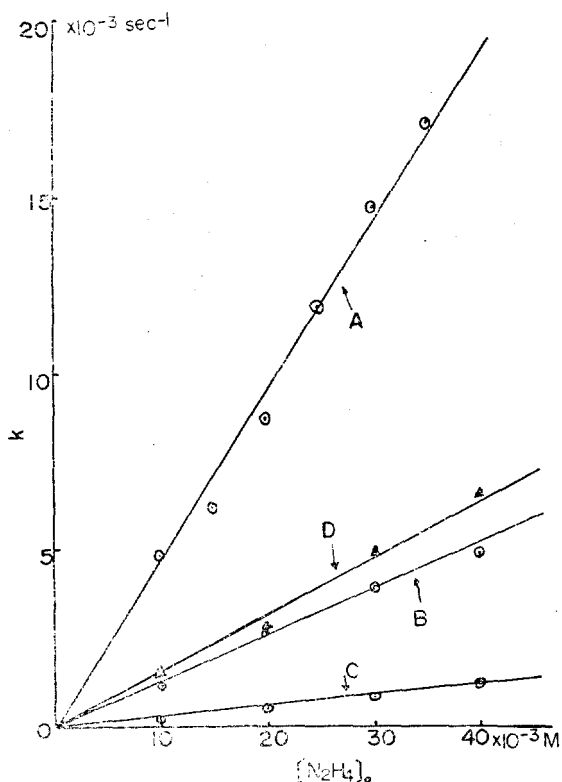


Fig. 3. Dependence of the rate constants of gas evolution (D) and iodine consumption (A, B, C) on excess hydrazine at $[N_2H_4]_0 = 10, 20, 30, 40 \times 10^{-3} M$, $[I_2]_0 = 0.97 \times 10^{-3} M$.

A & D $\begin{cases} [H^+] = 150 \times 10^{-3} M \text{ (pH 0.82)} \\ [I^-]_0 = 5 \times 10^{-3} M \end{cases}$

B $\begin{cases} [H^+] = 450 \times 10^{-3} M \text{ (pH 0.35)} \\ [I^-]_0 = 5 \times 10^{-3} M \end{cases}$

C $\begin{cases} [H^+] = 450 \times 10^{-3} M \text{ (pH 0.35)} \\ [I^-]_0 = 15 \times 10^{-3} M \end{cases}$

$$K_1(N_2H_5^+) = [N_2H_4][H^+], \quad K_1^{(2)} = 10^{-8}$$

and

$$K_2(N_2H_6^{2+}) = [N_2H_5^+][H^+], \quad K_2^{(2)} = 10^{0.3}$$

at 25 °C.

By differentiating eq. (6) with respect to pH,

$$\frac{d(N_2H_5^+)}{d(H^+)} = \frac{K_2(K_1K_2 - (H^+)^2) C_{N_2H_4}}{(K_1K_2 + K_2(H^+) + (H^+)^2)^2} \quad (7)$$

Thus, in the vicinity of pH=1, the concentration of single protonated hydrazine molecule increases almost linearly. Inspection of Fig. 5 with eq. (7) in mind suggests that the rate of consumption of iodine is first order in the concentration of neutral hydrazine molecule, since log k vs. pH plot has slope close to unity in the lower pH range, whereas it tends to a constant value which may correspond to the condition $C_{N_2H_4} = [N_2H_5^+]$;

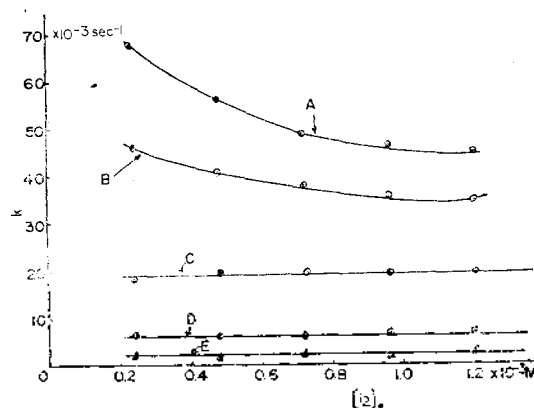


Fig. 4. Effect of small iodine concentration on the rate constants of gas evolution (E) and iodine consumption (A, B, C, D) at large excess hydrazine.

A $\begin{cases} [N_2H_4]_0 = 20 \times 10^{-3} M \\ [H^+] = 26 \times 10^{-3} M \text{ (pH 1.58)} \\ [I^-]_0 = 6.25 \times 10^{-3} M \end{cases}$

B $\begin{cases} [N_2H_4]_0 = 15 \times 10^{-3} M \\ [H^+] = 20.5 \times 10^{-3} M \text{ (pH 1.68)} \\ [I^-]_0 = 6.25 \times 10^{-3} M \end{cases}$

C $\begin{cases} [N_2H_4]_0 = 20 \times 10^{-3} M \\ [H^+] = 61.2 \times 10^{-3} M \text{ (pH 1.21)} \\ [I^-]_0 = 6.25 \times 10^{-3} M \end{cases}$

D $\begin{cases} [N_2H_4]_0 = 20 \times 10^{-3} M \\ [H^+] = 61.2 \times 10^{-3} M \text{ (pH 1.21)} \\ [I^-]_0 = 18.75 \times 10^{-3} M \end{cases}$

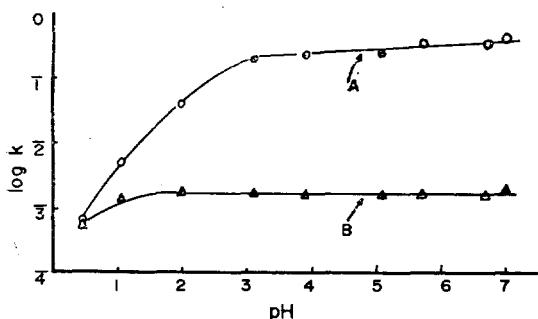
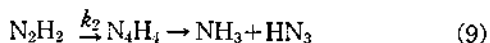
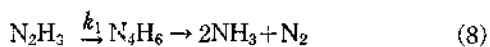


Fig. 5. Dependence of the rate constants of gas evolution (B) and iodine consumption (A) on pH at $[N_2H_4] = 15 \times 10^{-3} M$, $[I_2]_0 = 0.9 \times 10^{-3} M$, $[I^-]_0 = 5 \times 10^{-3} M$. B: Log k of gas evolution

$[N_2H_5^+]$ becomes maximum when $(H^+) = \sqrt{K_1 K_2} = 10^{-4.2}$. In view of the fact that the rate of gas evolution follows the similar pattern but it is three orders of magnitude smaller than the rate of iodine consumption when pH is higher than about 3, one can conclude that the gas evolution reaction is the slowest step and follows the iodine consumption reaction. Furthermore, under the conditions examined, only negligible amounts of ammonia and hydrazoic acid are formed, indicating that the extent of following reactions is very small.



Since $k_1^{(3)}$ is reported to be of the order of $10^9 M^{-1} \text{sec}^{-1}$ and the asymptotic value of the rate of iodine consumption in Fig. 5 is about $7 \times 10^{-3} M \text{sec}^{-1}$ ($\approx k(N_2H_4)_0$), the extent of formation of N_2H_3 must be negligible. Therefore, it can be postulated that the most provable mechanism is the reaction followed by to form an intermediate X which decomposes by⁽⁴⁾ a first order reaction. The intermediate X may well be $N_2H_2I_2$. The asymptotic rate constant of gas evolution of $1.5 \times 10^{-3} \text{sec}^{-1}$ in Fig. 4 is the rate constant of

the decomposition of the intermediate X. The greater values of the rate constant of gas evolution is observed in strongly acidic media¹ which suggests that decomposition of X is accelerated by proton.

Now, one can explain all the features noted in the figures. In the lower pH region, the rate of iodine consumption and the rate of the production of the intermediate X are comparable. Hence, the rate of gas evolution is governed by the rate of the production of X, when the pH is extremely low; eventually, the rates of the two process become the same when the rate determining step is the production of X. The behavior of the rate of iodine consumption shown in Fig. 4 suggests that there is involved a certain reversible process, although more detailed study is needed to draw more definite conclusion.

The agreement of the gas evolution rate reported in the previous report¹ and the rate of iodine consumption reported elsewhere⁴ is explained as accidental; namely, the above mentioned works were carried out in the low pH range where the production of the intermediate X is the rate determining step.

ACKNOWLEDGEMENT

The authors are grateful to the Ministry of Education for financial support provided to those at Chonnam National University.

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