DAEHAN HWAHAK HWOEJEE
(Journal of the Korean Chemical Society)
Vol. 18, No. 3, 1974
Printed in Republic of Korea

황산 산성용액에서 기체발생에 의한 $N_2H_4-I_2$ 반응속도

崔 柱 鉉

전남대학교 문리과대학 화학과

(1974. 3. 26 접수)

Gas Evolution Kinetics of $N_2H_4-I_2$ Reaction in a Sulfuric Acid Medium

Chuhyun Choe

Department of Chemistry, Chonnam National University, Kwang-ju Korea

(Received March 26, 1974)

요 약. 황산산성에서의 히드라진과 요오드의 반응에 대하여, 기체발생속도를 측정하였다. 이미 보고된 요오드의 소비속도의 경우와 마찬가지로, 히드라진 및 요오드의 농도에 관하여는 1차 반응이며, 반응속도는 요오드화이온의 농도에 역비례한다. 그뿐만 아니라, 요오드의 소비속도와 기체 발생속도가 거의 같으므로, 수명이 긴 중간물이 생기지 않는다고 결론지을 수 있다.

Abstract. The kinetics of gas evolution in the reaction between hydrazine and iodine in a sulfuric acid medium has been studied at 25 °C. The rate is first order in hydrazine and iodine concentration. The iodide ion retards the reaction whereas the effect of hydrogen ion concentration is rather complicated. The rate of gas evolution is very close to that of iodine consumption.

Introduction

It has been shown that hydrazine reacts with bromine extremely rapidly to form a certain intermediate which decomposes rather slowly[1]. Although the rate of consumption of iodine by hydrazine in a sulfuricacid medium has been studied[2], no study on the reaction products app eared in the literature. The results of kinetics studies of gas evolution in the same reaction is presented in this report.

Experimental

Reagents. Doubly distilled water and oxygen free nitrogen are prepared as described elsewhere[3]. The materials employed are of highest possible purity. Both iodine and hydrazine sulfate of AR grade are purified before use.

Procedure. The reaction vessel consists of a 250 m*l* Erlenmeyer flask with a ground stopper equipped with a gas injection tube and a delivery tube. After the reaction mixture except iodine is prepared in the reaction vessel, the lather is immersed in a thermostat kept at 25 °C. While agitating the mixture by means of a rotating magnetic bar, oxygen-free nitrogen is passed for at least twenty minutes to eliminate oxygen from the solution. The delivery tube is then connected to a U-tube manometer filled with water by using rubber tubing. After stopping the nitrogen flow, a measured volume of iodine solution is added as rapidly as possible and the pressure inside the vessel is made equal to the atmospheric pressure by using appropriate stopcocks and the pressure variation is recorded as time passes. The total volume of the reaction mixtureis taken in such a manner that the pressure reading at the end of the reaction is in the vicinity of 15 cm.

Results and Discussion

As shown in *Fig.* 1, the rate of gas evolution follows the first order kinetics when hydrazine is present in large excess. The first order rate constant is directly proportional to the concentration of hydrazine, whereas it is inversely proportional to the concentration of iodide ion. The iodine concentration will be reduced by the presence of iodide ion as given by the relationship

$$[I_2] \doteqdot \frac{C_{I_2}}{K(C_I - C_{I_2})} \tag{1}$$

where C_I and C_{I_2} represent the analytical concentration of iodide and iodine, respectively. Therefore the inverse proportional is expected to hold only when C_I is much greater than C_{I_2}. The results are shown in *Figs.* 2 and 3, respectively. The effect of hydrogen-ion concentration appears to be rather complicated, although, in a range of pH(0.98～1.35), an inverse proportional relationship has been reported[2]. Thus, in a narrow range of hydrogen-ion concentration, one can expect that the rate of the N_2H_4-I_2 reaction with respect to both the iodine consumption and the gas evolution is expressed in the form

$$\text{Rate} = K(N_2H_4)_0 \ [H^+]_0^n \ \frac{[I_2]}{[I^-]}. \tag{2}$$

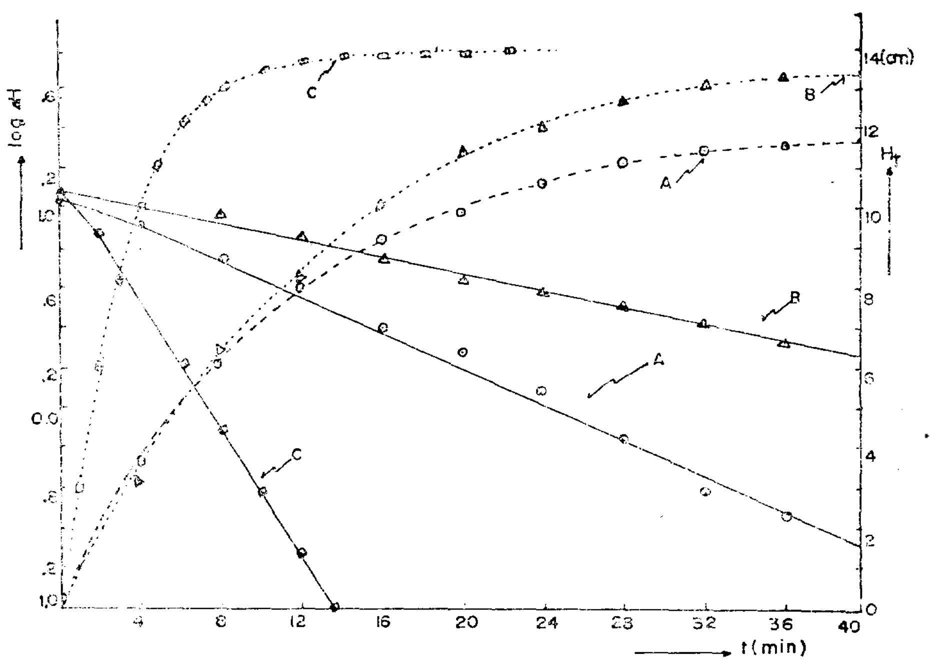

Fig. 1. Typical kinetic data of gas evolution in N_2H_4-I_2 reaction
—— : Log ΔH, ...:Gas evolution
A : $[N_2H_4]_0=15\times10^{-3}\,M$ $[H^+]=0.03\,M$ $C_{I_2}=0.96\times10^{-3}\,M$ $C_I=14.5\times10^{-3}\,M$
B : $[N_2H_4]_0=5\times10^{-3}\,M$ $[H^+]=0.02\,M$ $C_{I_2}=0.90\times10^{-3}\,M$ $C_I=10\times10^{-3}\,M$
C : $[N_2H_4]_0=40\times10^{-3}\,M$ $[H^+]=0.15\,M$ $C_{I_2}=0.95\times10^{-3}\,M$ $C_I=5\times10^{-3}\,M$

Thus, the rate constant k obtained from the experiments where the initial concentration of hydrazine largely exceeds that of iodine will be given by

$$k \doteqdot K^* [N_2H_4]_0 \ [H^+]_0^n \ \frac{1}{C_I} \qquad (3)$$

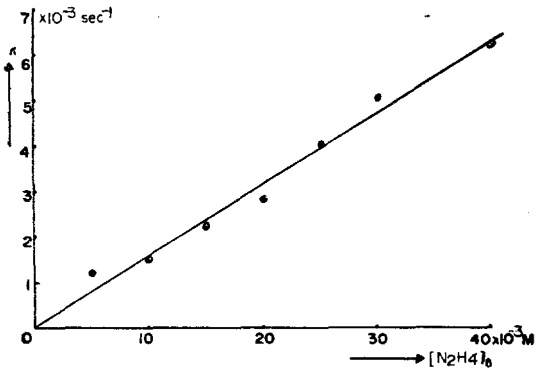

Fig. 2. Dependence of the rate constant on the initial concentration of hydrazine at $C_{I_2}=0.90\times10^{-3}$ M $[H^+]_0=0.15\,M$ $C_I=5\times10^{-3}\,M$

provided $C_I \gg C_{I_2}$ holds. Assuming $n=1$ for a narrow range of hydrogen concentration, the specific rate constant K^* can be computed from

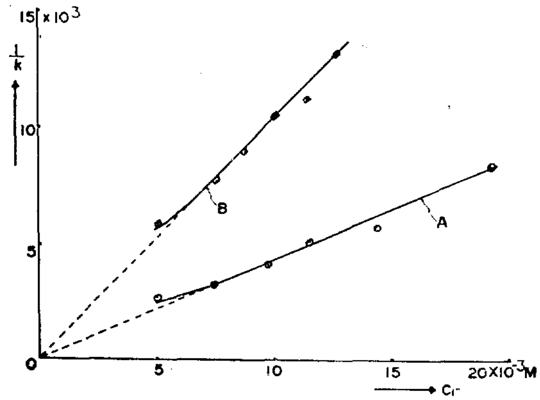

Fig. 3. Dependence of the rate constant on the concentration of iodide ion.
A : $[N_2H_4]_0=15\times10^{-3}\,M$ $C_{I_2}=0.96\times10^{-3}\,M$ $[H^+]_0=0.03\,M$
B : $[N_2H_4]_0=\ \times10^{-3}M$ $C_{I_2}=0.90\times10^{-3}\,M$ $[H^+]_0=0.02\,M$

Table 1. The first order rate constants and computed specific rate constants

	$[H^+]_0$ M	C_{I^-} $\times10^3\,M$	C_{I_2} $\times10^3\,M$	$[N_2H_4]_0\times10^3 M$	$k\times10^3$ sec^{-1}	$\frac{1}{k}$	K^* $\times10^3$
		4.83			3.71	269.9	3.82
		7.25			2.73	329.4	4.22
A	0.032	9.63	0.96	15.0	2.46	407.5	5.05
		14.49			1.62	538.0	4.89
		19.23			1.22	820.0	5.00
		5.00			1.84	605.2	3.86
		7.50			1.29	774.5	4.06
B	0.021	8.75	0.90	5.0	1.12	891.2	4.12
		10.00			0.97	1,035.0	4.07
		11.25			0.90	1,170.0	4.25
		12.50			0.77	1,302.6	4.04
				5.0	1.21		17.0
				10.0	1.47		10.3
				15.0	2.18		10.2
C	0.15	5.00	0.95	20.0	2.75		9.6
				25.0	4.03		11.3
				30.0	5.10		11.9
				40.0	6.23		10.9

the experimentally observed rate constants by using eq. (3). The results are summarized in *Table* 1. The constancy of the specific rate constant is remarkable. Furthermore, its order of magnitude is the same as that obtained from the reported results[2] of the studies on the iodine consumption. Consequently, it is concluded that there is no long lived intermediate formed in the reaction between hydrazine and iodine. In other words, the products of the $N_2H_4-I_2$ reaction react very rapidly to result in the final gaseous product. The production of small amounts of hydrazoic acid and ammonia in relatively slow reactions indicates that diimide is one of the intermediates of the reaction[4].

Acknowledgement

The author expresses his gratitude to Professor Q. W. Choi for suggesting the problem. He also thanks Mr. Won-Ki Choi and Mr. S. K. Lee for their technical assistance.

Literature Cited

1. Q. Won Choi, *et al.*, to be published.
2. Kalyan K. Sengupta and Samir K. Sengupta, *Z. Physik. Chem. N. F.*, **45**, 378(1965).
3. Q. Won Choi and Jin Jung, *This Journal*, **15**, 183(1971).
4. Chuhyun Choe, *et al.*, to be published.