Kinetic Studies of the Reaction of Nitrous Acid with Iodide Ion in the Presence of Molecular Oxygen in an Acid Solution

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The kinetics of the reaction between nitrous acid and iodide ion were studied in the presence of molecular oxygen (O_2) in an acid solution (pH 1.9—3.1); much larger amounts of the triiodide ion than expected from the amounts of nitrous acid were formed under conditions of the iodide ion in excess over nitrous acid. The initial rates for the formation of I_2 and I_3^- increased proportionally with increasing both the O_2 and nitrous acid contents, and increased greatly with decreasing the pH in the solution. The reaction rate was also decreased by bubbling either air or O_2 through the reacting solution, depending on the bubbling velocity. A chain mechanism is proposed to account for the results obtained in the dark: $2HNO_2+2I^-+2H^+ \longrightarrow 2NO+I_2+2H_2O$; $2NO+O_2 \longrightarrow 2NO_2$; $2NO_2 \rightleftharpoons N_2O_4$; $N_2O_4+2I^-+2H^+ \longrightarrow 2HNO_2+I_2$; $I_2+I^- \rightleftharpoons I_3^-$. The rate-determining step was the reaction of NO with O_2. The addition of trace amounts of copper(II) or iron(II) ion enhanced the formation of I_2 and I_3^- due to the occurrence of reactions of I^- with the metal ions. Such an acceleration effect by the metal ions, however, could be diminished by the addition of ethylenediaminetetraacetic acid. Although the rate of the reaction of HNO_2 with I^- was not greatly changed by the irradiation of visible light during the initial period of reaction, it was greatly accelerated after some formation of I_2 and I_3^-, being dependent on not only the light intensity, but also on the concentrations of H^+ and I^- ions. The effects of the metal ions as well as visible light are also accounted for by the above-mentioned mechanism.

Nitrous acid oxidizes iodide ions in an acid solution according to the following equation:[1)]

$$2HNO_2 + 2I^- + 2H^+ \longrightarrow 2NO + I_2 + 2H_2O. \quad (1)$$

Although the liberated iodine also reacts with nitrous acid, the reaction is very slow in acid solutions:[2)]

$$HNO_2 + I_2 + H_2O \longrightarrow NO_3^- + 2I^- + H^+. \quad (2)$$

Nitrous acid is a relatively weak acid of $pK_a = 2.95$ (25 °C and ionic strength $I = 0.09$—0.25 M, 1 M=1 mol dm^{-3}),[3)] and the rates of both reactions 1 and 2 are dependent on the hydrogen ion concentrations.[1,2)] It has been known that the removal of O_2 is most necessary and important for the determination of the concentrations of nitrite ions by using the nitrous acid–iodide reaction.[4)] We have presently found that although iodine could be quantitatively formed according to reaction 1 in the absence of molecular oxygen (O_2), it could be formed in the larger amounts than expected from the amounts of nitrite ion in the presence of O_2, and that the amounts of iodine formed are quite dependent on the concentrations of O_2. The mechanisms of the nitrous acid–iodide reaction in the presence of O_2 are discussed; it may be possible for the proposed reaction to be used for the determination of trace amounts of nitrite ions in aqueous solutions. Considering the redox potentials for the Cu^{2+}/Cu^+ and Fe^{3+}/Fe^{2+} redox couples in comparison to those of the I_2/I^- and $O_2/O_2^{-\bullet}$ ones, the effects of the copper(II) and iron(II) ions on the reaction are also very interesting. Since the products of the reaction, I_2 and I_3^-, are so sensitive to visible light as to yield the $I^\bullet$ radical,[5,6)] the effect of light on the reaction is also interesting.

Experimental

Materials. Potassium iodide, sodium nitrite, and the other chemicals used were of guaranteed grade of Wako Pure Chemical Industries, Ltd. All of the solutions used for measurements were freshly prepared by using redistilled water.

Procedure. Kinetic measurements were carried out by the previously reported method[5)] under the conditions of I^- in excess over NO_2^-. The temperature of the reaction solutions was controlled to within 0.1 °C. Aliquot solutions were taken out at appropriate time intervals after starting the reaction; the absorbance at 350 nm due to I_3^- was measured by a Shimadzu UV-150-02 spectrophotometer. For the light-irradiation experiments, two 100-W tungsten lamps were used. The light intensity was determined by a previously reported method.[6)] Gas-bubbling through the reacting solution considerably decreased the rate of iodine formation. Therefore, each solution containing I^- or HNO_2 was saturated separately with bubbling gas of oxygen, air, nitrogen, or argon through the solution before mixing the I^- and HNO_2 solutions; each gas was then continuously supplied to the surface of the solution during the reaction.

Results and Discussion

The iodine (I_2) formed during reaction 1 is rapidly converted to the triiodide ion (I_3^-) in the presence of I^-,

$$I_2 + I^- \rightleftharpoons I_3^-, \quad (3)$$

where $k_3 = 5.6\times10^9$ M^{-1} s^{-1} and k_3/k_{-3} (or K_3)$= 7.1\times10^2$ M^{-1}.[7,8)] The I_3^- ion has large molar absorption coefficients of 3.82×10^4 and 2.50×10^4 M^{-1} cm^{-1} at 288 and 350 nm,[5)] respectively, where the absorptions of I_2, NO_2^-, and HNO_2 were quite negligible. The concentrations of I_3^- were proportional to those of I_2 in the presence of I^- in large excess. Thus, the absorbance

of I_3^- could be used as a monitor for the kinetic measurements in this work. All of the kinetic runs were carried out under the conditions that the I^- ion was in at least 1000-fold excess over the I_2 formed by the reaction. Namely, the I^- ion was used in large excess over HNO_2.

Figure 1 shows plots of the absorbance of I_3^- at 350 nm against the reaction time for solutions saturated with four different gases. In an oxygen-free solution saturated with either Ar or N_2 gas, the absorbance after $t=1$ min maintained a constant value corresponding to the I_2 concentration formed by reaction 1. We confirmed that reaction 1 was completed within 10 s at $[I^-]=0.1$ M, $[NaNO_2]=1.0\times10^{-5}$ M at pH 2 under an Ar gas by the use of Photal RA-401 stopped-flow apparatus. The extrapolated values to $t=0$ for the three curves in Fig. 1 were almost identical to 0.063, which corresponds to the initial absorbance in the absence of O_2.

Dependence of Concentrations of HNO_2 and O_2. The initial rate for the formation of I_3^- (v_i) increased proportionally to the concentrations of added sodium nitrite (Fig. 2) as well as O_2 ($v_i=3.8\times10^{-8}$ $M s^{-1}$ in the air-saturated solution ($[O_2]=2.7\times10^{-4}$ M) and $v_i=2.0\times10^{-7}$ $M s^{-1}$ in the O_2-saturated solution ($[O_2]=1.4\times10^{-3}$ M)). The results given in Table 1 indicate that I_3^- (or I_2) is quantitatively formed for NO_2^- ions added in the absence of O_2, but is formed in much greater amounts than expected based on the amounts of the NO_2^- ion initially added in the presence of O_2, being quite dependent on the concentrations of O_2. This indicates that a chain reaction induced by O_2 must occur successively after the occurrence of the fast reaction given by Eq. 1.

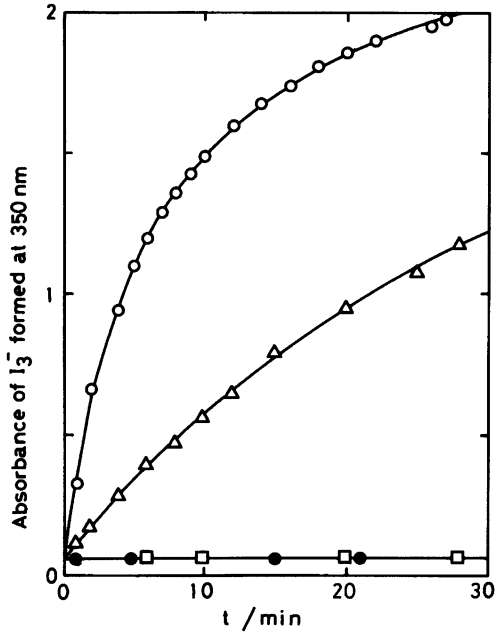

Fig. 1. Change in the absorbance of the I_3^- ion formed. Conditions: 5×10^{-6} M $NaNO_2$, 0.1 M KI, 0.01 M HNO_3, and pH 2.1 in the dark at 25 °C. ○: saturated with O_2, △: saturated with air, □: saturated with Ar, and ●: saturated with N_2.

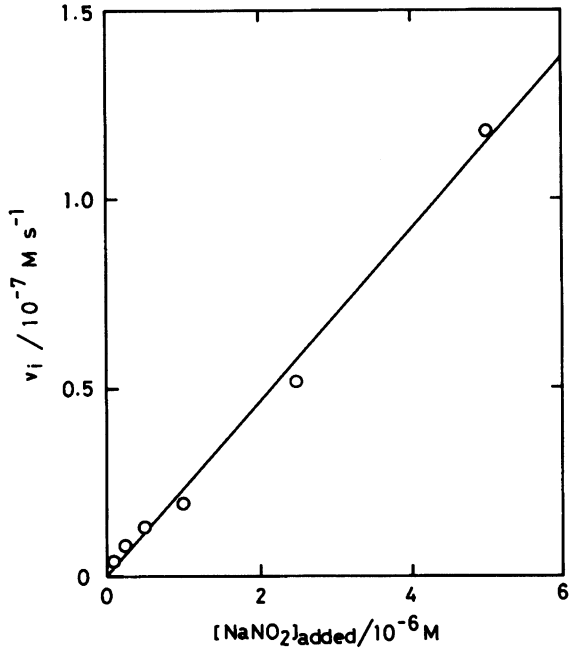

Fig. 2. Plots of v_i vs. $[NaNO_2]_{added}$ for the formation of I_3^- in the O_2-saturated solutions. The conditions are the same as in Fig. 1.

Table 1. Effect of Concentrations of Nitrite Ion on the Formation of Triiodide Ion[a)]

$[NO_2^-]_{added}/10^{-6}$ M	$[I_3^-]_{formed}/10^{-5}$ M		
	N_2-Sat.	Air-Sat.	O_2-Sat.
0.1 (4.6 ppb)	—	—	0.018[b)]
0.1	—	—	0.039[c)]
0.1	—	—	0.126
0.25	—	—	0.380
0.50	—	—	0.664
1.0	0.060	—	1.22 1.11
2.5	0.14	1.33	2.66 2.48
5.0	0.24	3.80	7.18 7.44
5.0	0.24[b)]	0.68[b)]	2.64[b)]
5.0	0.24[c)]	1.12[c)]	3.76[c)]
10.0	0.50	—	6.15[b)]

a) $t=20$ min. The other conditions are the same as in Fig. 1. b) $t=2$ min. c) $t=4$ min.

Effect of the Iodine Concentration. The addition of I_2 (up to 5×10^{-5} M) did not affect the rate of formation of I_3^- in the reaction of HNO_2 and I^- in the presence of O_2 at pH 1.85, indicating no contribution of the backward reaction of Eq. 6.

Effect of Acid, pH, and Concentration of I^-. The rate of formation of I_3^- in the presence of O_2 increased with increasing concentrations of either H^+ or I^-, and was similar to each other in HCl, HNO_3, and H_2SO_4 solutions (see Fig. 3 and Table 2). Figure 3

Table 2. Effect of Acid and the Concentrations of Iodide Ion on the Triiodide Ion Formation at $t=30$ min[a)]

$[I^-]_{added}$/M	$[I_3^-]_{formed}/10^{-5}$ M					
	HNO_3		HCl		H_2SO_4	
	pH=3.0	pH=2.1	pH=3.1	pH=2.1	pH=2.85	pH=1.9
0.001	0	—	—	—	—	—
0.005	0.088	—	—	—	—	—
0.01	0.252	—	—	—	—	—
0.025	1.06	—	0.87	—	1.58	—
0.05	1.80	—	1.70	—	2.67	1.12[d)]
0.10	2.87	4.80 8.0[b)]	2.74	7.88[b)]	3.62	7.60[b)]
0.10	—	2.84[c)]	—	3.08[c)]	—	3.22[c)]
0.10	—	1.80[d)]	—	1.42[d)]	—	1.59[d)]
0.20	—	—	—	—	—	1.84[d)]

a) In the air-saturated solution containing 0.001 or 0.01 M acids and 5.0×10^{-6} M $NaNO_2$ at 25 °C in the dark. b) As in a), but in the O_2-saturated solution. c) As in b), but 2.5×10^{-6} M $NaNO_2$. d) As in c), but in the air-saturated solution.

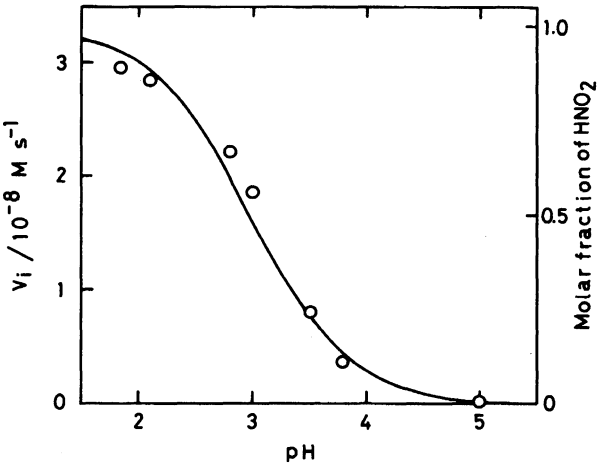

Fig. 3. Plots of v_i vs. pH in the air-saturated solutions. The solid curve is the pH dependence of the molar fraction of HNO_2. The conditions are the same as those in Fig. 1

shows that the reacting species is HNO_2, and that the amounts of NO produced in reaction 1 depends on the concentrations of HNO_2. The reaction rate above pH 4 became extremely slow, even in the presence of O_2. For example, the concentration of I_3^- formed at pH 4.2 in an air-saturated solution of 1.0×10^{-4} M $NaNO_2$ and 0.1 M KI was, even at $t=60$ min, only 1.0×10^{-5} M. The larger concentrations of I^- could increase the formation rate of I_3^- (see Table 2), indicating the contribution of the forward reaction of Eq. 1 and/or Eq. 6.

Temperature Dependence. The temperature dependence on the initial rate of the formation of I_3^- by the HNO_2–I^- reaction was examined at 5—40 °C under the same conditions as in Fig. 1. The results are given in Table 3. The values of $\Delta H^\ddagger=2.6$ kJ mol^{-1} and $\Delta S^\ddagger=-190$ J K^{-1} mol^{-1} obtained from the Eyring plot correspond to the second step of the reaction between

Table 3. Temperature Dependence on the Second Step of the Reaction between HNO_2 and I^- in the Presence of O_2[a)]

Temp	$[O_2]$	v_i	$v_i/([O_2][HNO_2]_i)$
°C	10^{-4} M	10^{-8} M s^{-1}	10 M^{-1} s^{-1}
5	4.2	2.7	1.3
10	3.7	3.3	1.8
25	2.7	3.3	2.4
40	2.2	3.6	3.3

a) Conditions are as plots △ of the air-sat. in Fig. 1. $\Delta H^\ddagger=2.6$ kJ mol^{-1} and $\Delta S^\ddagger=-190$ J K^{-1} mol^{-1}.

HNO_2 and I^-, where reaction 4 in the second step may be mainly responsible for the temperature dependence.

Bubbling Effect. When either air or O_2 gas was bubbled through the reaction solutions, the rate of formation of I_3^- changed greatly, being dependent on the bubbling velocity. The results of the air-bubbling effect are given in Fig. 4. Strong bubbling (70 ml s^{-1}) resulted in similar results to those in the absence of O_2. Such a fact indicates that a chain-carrier gas in the HNO_2–I^- reaction could be removed by bubbling gas through the solution, where the chain-carrier gas would be NO, NO_2, or N_2O_4 in the mechanism of proposed reaction (vide infra).

Effect of Radical Scavengers, Ethanol, and Metal Salts. Although acrylamide, acrylonitrile, ethanol, and zinc(II) sulfate did not seriously affect the formation of I_3^-, copper(II) sulfate, iron(II) sulfate, and large amounts of calcium(II) nitrate and potassium nitrate increased the formation of I_3^- (see Fig. 5 and Table 4). Although the effect of copper(II) and iron(II) is very large, it completely diminished upon the addition of ethylenediaminetetraacetic acid.

Effect of Light. Although the effect of light was not appreciable during the initial period of the reaction, the formation rate of I_3^- after some reaction time

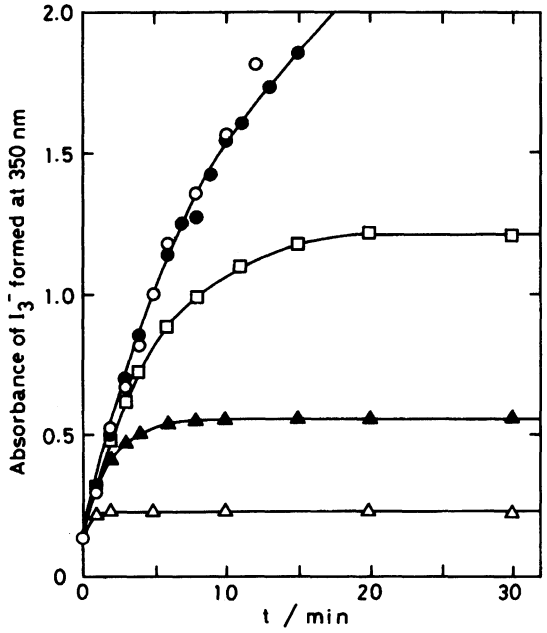

Fig. 4. Effect of gas-bubbling through the solution. The conditions are the same as those in Fig. 1, except for 1.0×10^{-5} M $NaNO_2$ for the air to be bubbled through the solution with a constant velocity of 0.13, 4.7, 14, and 70 $ml\,s^{-1}$ for plots ●, □, ▲, and △, respectively. Plots ○ indicate the results without bubbling air through the solution.

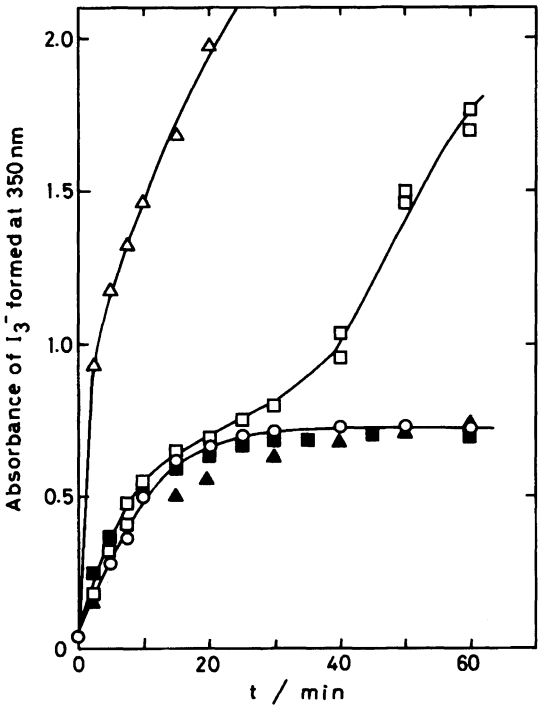

Fig. 5. Effect of Cu^{2+} and Fe^{2+} ions in an O_2-saturated solution containing 2.5×10^{-6} M $NaNO_2$. The other conditions are the same as in Fig. 1. ○: without additives, △: ○+1.0×10^{-4} M $CuSO_4$, ▲: △+1.0×10^{-4} M ethylenediaminetetraacetic acid, □: ○+1.0×10^{-4} M $FeSO_4$, and ■: ○+1.0×10^{-4} M ethylenediaminetetraacetic acid.

increased with an increase in the irradiated light intensity (I_0, see Fig. 6). The light effect was indifferent to any acid of HNO_3, HCl, or H_2SO_4. Further, even in the absence of NO_2^-, an increase in the concentrations of I_3^- was observed upon light irradiation in the presence of I_2 or I^- during the initial stage of the reaction, being dependent on the I^- concentrations. The effect of light was greatly dependent on the concentrations of not only H^+, but also I^-, and diminished at either 0.01 M KI or 0.001 M H_2SO_4 (see Fig. 6).

Mechanism of Reaction. All of the results obtained in the dark can be accounted for by the following mechanism:

$$2HNO_2 + 2I^- + 2H^+ \xrightarrow{\text{fast}} 2NO + I_2 + 2H_2O, \quad (1)$$

$$2NO + O_2 \xrightarrow{\text{slow}} 2NO_2, \quad (4)$$

$$2NO_2 \rightleftharpoons N_2O_4, \quad (5)$$

$$N_2O_4 \text{ (or } 2NO_2) + 2I^- + 2H^+ \rightleftharpoons 2HNO_2 + I_2, \quad (6)$$

$$I_2 + I^- \rightleftharpoons I_3^- \qquad [K_3 = 7.1\times10^2\ M^{-1}], \quad (3)$$

and

$$HNO_2 \rightleftharpoons NO_2^- + H^+ \qquad [K_a = 1.1\times10^{-3}\ M]. \quad (7)$$

The rate of the forward reaction of Eq. 1 increased upon increasing the H^+ concentrations as well as the I^- ions, and became extremely slow at pH values larger than 3.5. Therefore, the chain reaction mentioned above could operate only below pH 3, where most nitrite ions exist as the acid form of HNO_2. Ferranti et al.[1] reported on the kinetics of reaction 1, which was second-order with respect to the concentrations of HNO_2, I^-, and H^+, and proposed the following elementary steps:

$$H^+ + HNO_2 \rightleftharpoons H_2NO_2^+, \quad (8)$$

$$H_2NO_2^+ + I^- \rightleftharpoons NOI + H_2O, \quad (9)$$

and

$$2NOI \longrightarrow 2NO + I_2. \quad (10)$$

The most important and necessary reaction to make the chain reaction due to O_2 is Eq. 4. The initial rate of the reaction increases proportionally to the concentrations of O_2 and NO. The concentration of NO is proportional to that of added nitrite ions. Therefore, the rate-determining step in reaction 4 is the reaction of NO and O_2.

The gases of NO, NO_2, and N_2O_4 are among the chain-carriers for the entire reaction, but are capable of being removed by bubbling any gas of air or oxygen through the reacting solution. Consequently, the formation rate of the triiodide ion greatly decreased upon bubbling either air or oxygen, depending on the bub-

Table 4. Effect of Radical Scavengers, Ethanol, and Metal Salts[a)]

Substances added	$[I_3^-]_{formed}/10^{-5}$ M		
	t=10 min	t=30 min	t=60 min
None	0.80	1.80	2.76
Acrylamide			
1.0 wt%	0.80	1.76	2.72
1.5 wt%	0.80	1.82	2.78
Acrylonitrile			
1.0 vol%	0.80	1.59	2.66
1.5 vol%	0.68	1.58	2.40
2.5 vol%	0.80	1.59	2.72
Ethanol			
12 vol%	0.72	1.75	2.64
15 vol%	0.89	1.97	2.96
$ZnSO_4 \cdot 6H_2O$			
3.5×10^{-4} M	0.80	1.80	2.63
3.4×10^{-1} M	0.96	2.07	3.08
$Ca(NO_3)_2 \cdot 4H_2O$			
8.5×10^{-4} M	1.00	1.73	2.75
4.24×10^{-1} M	1.50	2.86	4.10
KNO_3			
1.0 M	1.90	3.78	4.64
1.5 M	2.20	5.31	6.26

a) In the air-saturated solutions containing 2.5×10^{-6} M $NaNO_2$. The other conditions are the same as in Fig. 1.

bling rate (Fig. 4).

All of the results obtained in the present study could be likely by considering the following redox potentials[9)] for each reaction:

$$I_2 + 2e^- \rightleftharpoons 2I^- \quad [E^0 = 0.54\ V], \quad (11)$$

$$HNO_2 + H^+ + e^- \rightleftharpoons NO + H_2O \quad [E^0 = 1.00\ V], \quad (12)$$

and

$$N_2O_4 + 2H^+ + 2e^- \rightleftharpoons 2HNO_2 \quad [E^0 = 1.07\ V]. \quad (13)$$

It is noted that reaction 6 can be written in terms of the three elementary reactions as follows:

$$NO_2 + I^- \rightleftharpoons NO_2^- + I^\cdot, \quad (14)$$

$$I^\cdot + I^- \rightleftharpoons I_2^{-\cdot}, \quad (15)$$

and

$$NO_2 + I_2^{-\cdot} \rightleftharpoons NO_2^- + I_2, \quad (16)$$

where $K_{14}<1.14\times10^{-3}$, $k_{-14}=8.8\times10^9\ M^{-1}\,s^{-1}$, $K_{15}=1.03\times10^4\ M^{-1}$, and $k_{15}=9.8\times10^9\ M^{-1}\,s^{-1}$.[10)] Reaction 6 corresponds to an overall reaction of Eqs. 14, 15, and 16. It is noted that the backward reactions of Eqs. 14, 15, and 16 could not easily occur under the conditions of relatively high concentrations of I^- and H^+. The termination reactions for the chain reaction given above may be as follows:

$$NO_2^- + 2I_2^{-\cdot} + H_2O \longrightarrow NO_3^- + 4I^- + 2H^+, \quad (17)$$

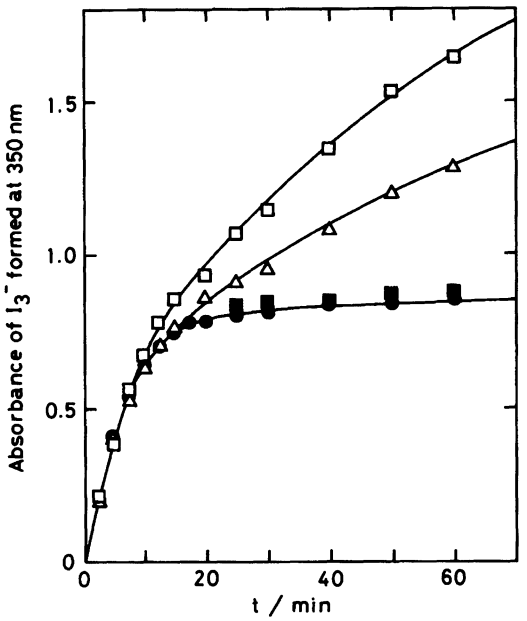

Fig. 6. Effect of light in O_2-saturated solutions at $[NaNO_2]=2.5\times10^{-6}$ M, [KI]=0.1 M, $[H_2SO_4]=0.01$ M (pH 1.9), and 25 °C. ●: in the dark, △: $I_0=1.13\times10^{-7}\ M\,s^{-1}$, □: $I_0=2.26\times10^{-7}\ M\,s^{-1}$, ■: $[H_2SO_4]=0.001$ M (pH 2.85) and $I_0=2.26\times10^{-7}\ M\,s^{-1}$.

$$2HNO_2 + O_2 \longrightarrow 2NO_3^- + 2H^+, \quad (18)$$

and

$$4NO_2 + 2H_2O + O_2 \longrightarrow 4NO_3^- + 4H^+. \quad (19)$$

Reactions 18 and 19 compete to reactions 1 and 6, respectively, and, thus, could not occur likely under the condition that $[I^-] \gg [O_2]$.

Although iodide ion oxidation to I_2 with nitric acid was not observed under the conditions of Fig. 1 (i.e., at 0.01 M HNO_3) within 1 h, it was appreciable for greater than two hours of reaction time, and was also appreciable for solutions of higher concentrations of nitrate, such as 1.0 and 1.5 M KNO_3 (Table 4). This would be likely considering the following redox potentials:[9)]

$$2NO_3^- + 4H^+ + 2e^- \rightleftharpoons N_2O_4 + 2H_2O \quad [E^0 = 0.80\ V] \quad (20)$$

and

$$NO_3^- + 3H^+ + 2e^- \rightleftharpoons HNO_2 + H_2O \quad [E^0 = 0.94\ V]. \quad (21)$$

According to the redox couples of Eq. 11 with Eq. 20 or Eq. 21, the occurrence of the oxidation of I^- to I_2 with NO_3^- causes the formation of N_2O_4 or HNO_2, and thus, could participate in a chain reaction of Eqs. 1, 4, 5, and 6. Therefore, the addition of large amounts of potassium nitrate or calcium nitrate into the solution could increase the rate of the triiodide ion formation.

The effect of the copper(II) ion can be accounted for by a simultaneous and additional occurrence of the following reactions to reactions 1, 4, 5, and 6:

$$4I^- + 2Cu^{2+} \longrightarrow I_2 + 2CuI, \quad (22)$$

$$CuI \rightleftharpoons Cu^+ + I^- \quad [K = 1.1 \times 10^{-12}\ M],^{9)} \quad (23)$$

$$CuI\ (\text{or } Cu^+) + O_2 \rightleftharpoons Cu^{2+} + I^- + O_2^{-\cdot}, \quad (24)$$

$$O_2^{-\cdot} + H^+ \rightleftharpoons HO_2^{\cdot} \quad [pK_a \text{ of } HO_2^{\cdot} = 4.8],^{11)} \quad (25)$$

$$2HO_2^{\cdot} + 2I^- + 2H^+ \longrightarrow I_2 + 2H_2O_2, \quad (26)$$

and

$$H_2O_2 + 2I^- + 2H^+ \longrightarrow I_2 + 2H_2O. \quad (27)$$

The above reactions are likely to occur in relatively strong acid solutions containing relatively high concentrations of I^- by considering the following redox potentials[9] with Eq. 11:

$$Cu^{2+} + I^- + e^- \rightleftharpoons CuI \quad [E^0 = 0.86\ V], \quad (28)$$

$$HO_2^{\cdot} + H^+ + e^- \rightleftharpoons H_2O_2 \quad [E^0 = 1.50\ V], \quad (29)$$

and

$$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O \quad [E^0 = 1.77\ V]. \quad (30)$$

No precipitation of CuI was found in the reacting solution under the present experimental conditions. This is probably due to the slow coagulation of the CuI molecule as well as the rapid oxidation of CuI by reaction 24. Reactions 22—27 could occur to produce I_2 and I_3^-. Actually, the formation of I_3^- could be observed by the reaction between Cu^{2+} and I^-, even in the absence of NO_2^- (Fig. 7). After the rapid formation of I_2 and I_3^- due to reaction 22 (see lines (4), (5), and (6) in Fig. 7), the rate increases proportionally to the O_2 concentration, indicating the existence of reaction 24 followed by reactions 25—27. It was confirmed that reaction 22 could be retarded by the addition of ethylenediaminetetraacetic acid. The existence of reaction 27 was also confirmed by the result that H_2O_2 reacted with I^-, as shown in Fig. 8. In the case of Fe^{2+}, after Fe^{2+} had been oxidized to Fe^{3+} by the oxidizing species NO_2 and/or O_2, the Fe^{3+} ion formed in situ could enhance the I_3^- formation in the same way as in the case of Cu^{2+} (the plots □ in Fig. 5 and lines (1)—(3) in Fig. 7):

$$2I^- + 2Fe^{3+} \rightleftharpoons I_2 + 2Fe^{2+} \quad [K = 4.4 \times 10^3\ M^{-1}].^{12)} \quad (31)$$

The effect of light could be accounted for by the successive occurrence of the following reactions after the formation of I_2 according to reactions 1, 4, 5, and 6, which are indifferent to visible light:

$$I_2 \overset{h\nu}{\longrightarrow} 2I^{\cdot}, \quad (32)$$

$$I_3^- \overset{h\nu}{\longrightarrow} I_2^{-\cdot} + I^{\cdot}, \quad (33)$$

and

$$I^{\cdot} + I^- \rightleftharpoons I_2^{-\cdot}. \quad (15)$$

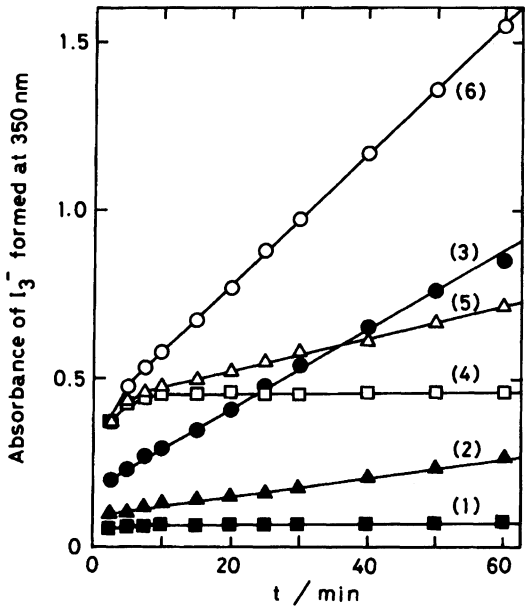

Fig. 7. Formation of I_3^- by the reaction of I^- with Cu^{2+} (5.0×10^{-5} M, open circle) or Fe^{3+} (1.0×10^{-5} M, closed circle) at [KI]=0.1 M, [HNO_3]=0.01 M (pH 2.1), and 25 °C in the dark. (1), (4) N_2-saturated, (2), (5) air-saturated, and (3), (6) O_2-saturated.

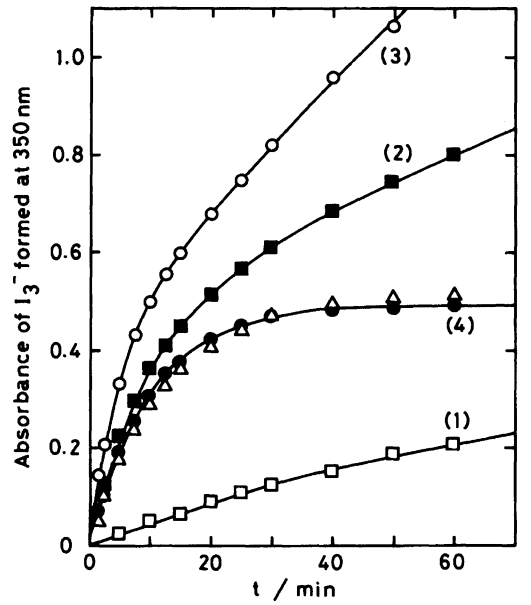

Fig. 8. Formation of I_2 and I_3^- by the reaction between I^- and H_2O_2 in air-saturated solutions containing 2.0×10^{-5} M H_2O_2, 0.01 M H_2SO_4 (pH 1.9), and $I_0 = 2.26\times10^{-7}$ M s^{-1}. (1) 0.01 M KI, (2) 0.1 M KI, (3) 0.2 M KI, and (4) ●: at 0.1 M KI in the dark and △: at 0.1 M KI and 0.001 M H_2SO_4 (pH 2.85).

Reaction 32 is practically the same as reaction 33,[10] as long as the forward reaction rate of Eq. 15[10] is rapid. Successively, after the formation of the $I_2^{-\cdot}$ species by light irradiation, reactions 16, 25, 26, and 27 would oc-

cur to accelerate the formation of I_3^- in the same way as in the case of the Cu^{2+} and Fe^{2+} effects.

The backward reactions of Eqs. 24 and 25 compete to the forward reaction of Eqs. 25 and 26, respectively. Actually, the light effect was rather dependent upon both the concentrations of H^+ and I^- and diminished at either pH>3 or $[I^-] \leqq 0.01$ M. Namely, the occurrence of reactions 25—27 is necessary for any effects of the metal ions (Cu^{2+} and Fe^{2+}) and light, and are only possible under the conditions of relatively high concentrations of H^+ and I^-. The formation of I_2 and I_3^- by the reaction between I^- and H_2O_2 (Eq. 27) was accelerated by the irradiation of visible light, as well as by increasing the concentrations of H^+ and I^- (Fig. 8).

Application to the Determination of Trace Amounts of Nitrite Ions. The removal of O_2 is most necessary for the determination of the concentrations of nitrite ions by using reaction 1.[4] However, our results demonstrate that it is not necessary to remove O_2 from solution, and that the amounts of iodine formed in the presence of O_2 are much larger than those in the absence of O_2. The absorbance at 350 nm at t=40 min, after which time the absorbance was constant due to the occurrence of the termination reaction, was proportional to the concentrations of nitrite ions added under the conditions that $[NaNO_2]_{added}=0—5.0\times10^{-5}$ M and $[KI]_{added}=0.1$ M at pH=2.1 (HNO_3) and 25 °C in the O_2-saturated solutions in the dark. The coefficient of the variation for 10 determinations at $[NaNO_2]_{added}=1.0\times10^{-7}$ M (4.6 ppb), for example, was 6.3% ($A_{350}=0.032\pm0.002$). It is possible to detect 1 ppb of NO_2^- ions by using the present method, and the detection limit for NO_2^- is much lower than that in the absence of O_2.

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