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KINETIC STUDIES ON THE OXIDATION OF SODIUM FORMATE IN TRIIODIDE AQUEOUS SOLUTION

By

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Abstract

The rate of the oxidation of formate in the triiodide aqueous solution were measured under the condition of pH 4–9, for the purpose of clarifying the source of oxidizing effect of oxidation reactions in the iodine aqueous solution. The rate equation was obtained, that is, rate$=k[I_3^-][HCOO^-]/([I^-]+b)$, where k and b were as follows: at 25°C, $k=0.334\times10^{-2}$ min^{-1}, $b=1.19\times10^{-3}$ M; at 30°C, $k=0.536\times10^{-2}$ min^{-1}, $b=1.71\times10^{-3}$ M; at 35°C, $k=1.21\times10^{-2}$ min^{-1}, $b=1.84\times10^{-3}$ M. b is a good agreement with the equilibrium constant for $I_3^-\rightleftarrows I_2+I^-$. The activation energy of this reaction was 21 kcal. The mechanism of this reaction and the intermediate complex were discussed.

Introduction

It has been known that the aldehydes and the sugars are oxidated in the iodine aqueous solution. The mechanisms were proposed by many workers that the source of the oxidizing effect was molecular iodine, hypoiodous acid, or atomic iodine. For example, DHAR[1)] and DOOSAY AND BHAGWAT[2)] proposed that in the oxidation reaction of sodium formate in an iodine aqueous solution, the rate was followed by the equation:

$$v=k[HCOO^-][I_2]$$

But it is not clarified whether the iodine molecule is the source of the oxidizing effect, or not, because the effect of iodide ion used and pH was not studied. INGLES AND ISRAEL[3)] and NAKAMURA[4)] proposed that in the oxidation reaction of aldose in alkaline solution of iodine, the source of the oxidizing effect was a hypoiodous acid. GRIFFITH AND MCKEOWN[5)], and ABEL AND HILFERDING[6)] proposed that in the reaction between iodine and oxalic acid, the hypoiodous acid and the iodine atom act as the oxidizing species. CHOW[7)] discussed the relationship between the rate of reaction and the oxidation-reduction potential of the reaction system. HAMMICK AND ZVEGINTZOV[8)] studied the rate of reaction between formic acid and iodine in acidic aqueous solution, and proposed the rate equation as follows:

$$v=k[HCOO^-][\Sigma I_2]/[I^-]/K_1$$

where ΣI_2 was the total concentration of free iodine (I_2 and I_3^-) and K_1 was the equilibrium constant of $I_3^-\rightleftarrows I_2+I^-$. But it is a problem that they did not considered that in an acidic aqueous solution the iodide ion is oxidized to iodine molecule. Recently, HILLER AND KRUEGER[9)] reported the rate and mechanism of the iodine-formate reaction in dimethyl sulfoxide-water solvents. They also studied the isotope effect between $HCOO^-$ and $DCOO^-$. They did not study the effect of the concentration of hydrogen ion.

It is the purpose of this paper to report a rate equation of the oxidation reaction between pH 4 and 9, and a discussion of the source of oxidizing effect. The stoichiometry of this reaction is $I_3^- + HCOO^- \rightarrow CO_2 + H^+ + 3I^-$.

Experimental

Reagents: Iodine, potassium iodide, and sodium formate were obtained commercially (all GR). Iodine was purified by the sublimation. The other reagents were weighed directly. The iodine solution was prepared by dissolving a weighed quantity of purified iodine in a buffer solution containing potassium iodide of a desired concentration. The solution of 0.2M (f=0.980) sodium formate was stocked. In all experiments, the potassium iodide and the sodium formate were present in excess sufficient to eliminate perturbations due to the iodide ion produced and the decomposition of formate during the reaction, respectively.

Kinetic measurements: Before mixing the reactants, the solutions were equilibrated for half an hour in the thermostat. The rate was followed by two methods under a constant temperature. The first was a back titration method. A constant volume of solution of the reaction system was pipetted and was added into a known concentration of sodium thiosulfate solution at different times. Then an excess of sodium thiosulfate solution was titrated by a standard solution of iodine. This method titrates the total iodine (I_2, I_3^-, IO^-, IO_2^-, IO_3^- etc.). The second was a spectrophotometric method. It was measuring the absorbance at 350 nm using a Hitachi 101 spectrophotometer at different times. At 350 nm, the molar extinction coefficient of triiodide ion is much larger than those of the iodine molecule and the hypoiodide ion. Except when the low concentration of iodide ion and the high concentration of hydroxide ion were employed in the aqueous runs, the iodine is essentially completely converted to the triiodide ion. Since the analogous iodine-oxalate reaction is known to proceed in part *via* a photoinitiated radical process,[5),10)] the effect of 350nm radiation was examined in several of the kinetic runs. One of two identical solutions was exposed only long enough to obtain several absorbance values, while the second solution was exposed continuously at 350 nm. A continuously exposed run decreased absorbance a little faster than a intermittently exposed run. Then rate measurements were obtained by exposing only long enough to obtain several absorbance values. All measurements were obtained in the dark room.

The effect of carbonate ion is studied by adding the sodium carbonate to the reactants solution. Consequently, the carbonate ion has no effect on the rate of the oxidation reaction of the formate.

Results

Fig. 1 indicates the plots of the logarithms of total concentration of iodine ($[\Sigma I_2]$) versus time. This $[\Sigma I_2]$ is the total concentration of iodine determined by the back titration

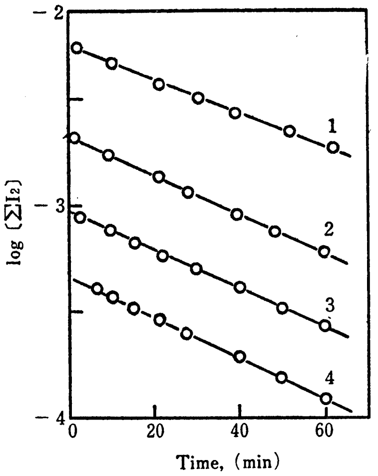


Fig. 1. Effect of the initial concentration of iodine on the rate (30°C). Concentration of the total iodine (ΣI_2) versus time plots. HCOONa 0.129 M; KI 0.03M; Initial concentration of iodine, (1) 4.68, (2) 9.46, (3) 21.5, and (4) 58.0×10^{-3} M. pH 6.

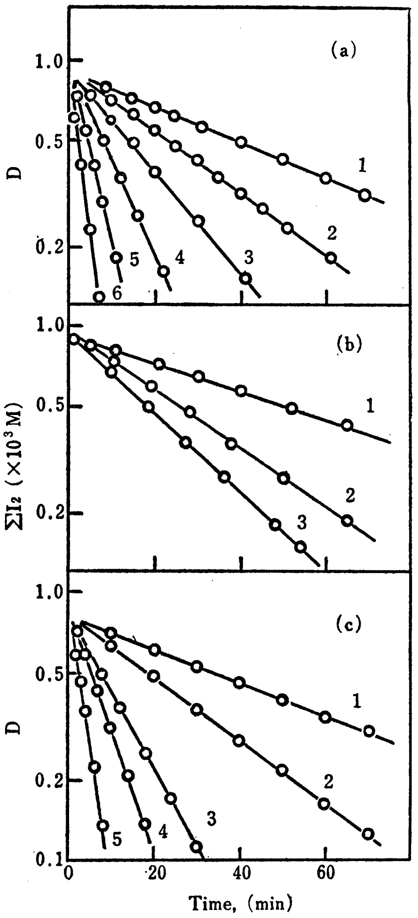


Fig. 2. Effect of concentration of formate on the rate. Absrobance (D) or concentration of total iodine (ΣI_2) versus time plots.

(a) 25°C; pH 7; KI 0.001 M; HCOONa (1) 0.014, (2) 0.025, (3) 0.04, (4) 0.08, (5) 0.14, and (6) 0.3 M.

(b) 30°C; pH 7; KI 0.03M; HCOONa (1) 0.07, (2) 0.15, and (3) 0.20 M.

(c) 35°C; pH 7; KI 0.002 M; HCOONa (1) 0.004, (2) 0.008, (3) 0.02, (4) 0.04, and (5) 0.10 M.

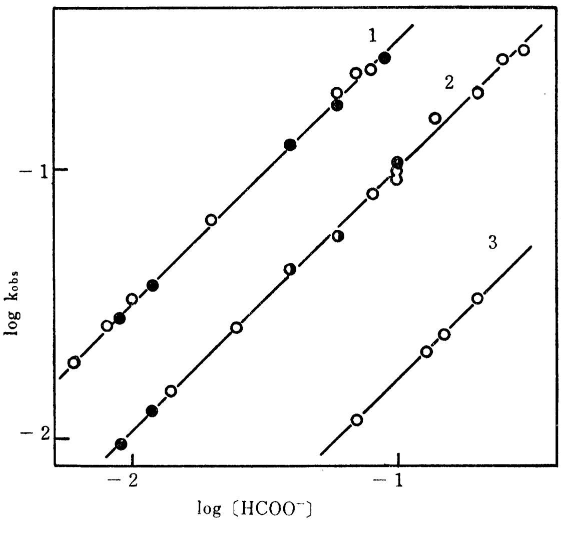


Fig. 3. Relation between the apparent first order rate constant k_{obs} and the concentration of formate [HCOO⁻]. Log k_{obs} versus log [HCOO⁻] plots. (1) 35°C, KI 0.002 M, pH 7 (○), and 5 (●). (2) Open circle, 25°C, KI 0.001 M, pH 7; Closed circle, 35°C, KI 0.01 M, pH 7. (3) 30°C, KI 0.01 M, pH 6.

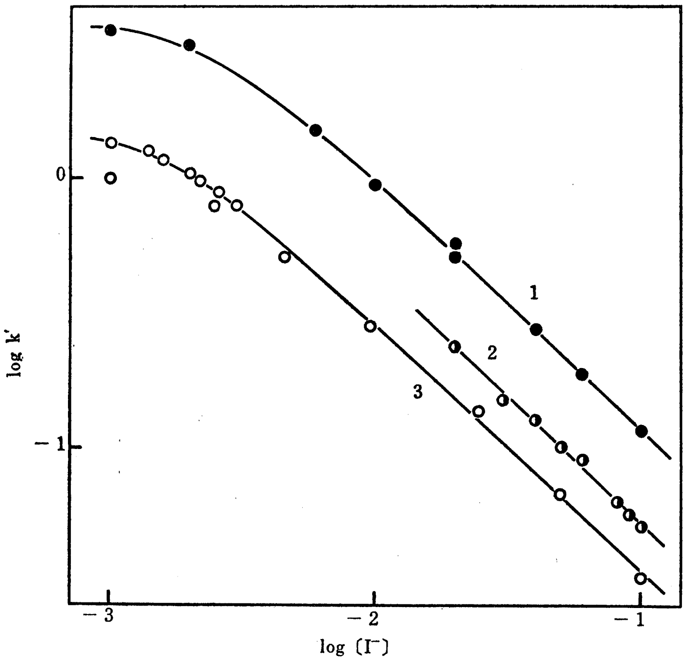


Fig. 4

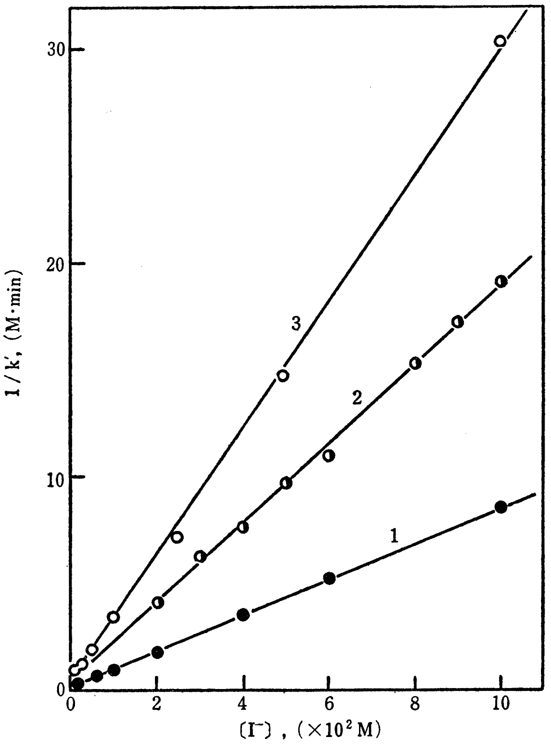
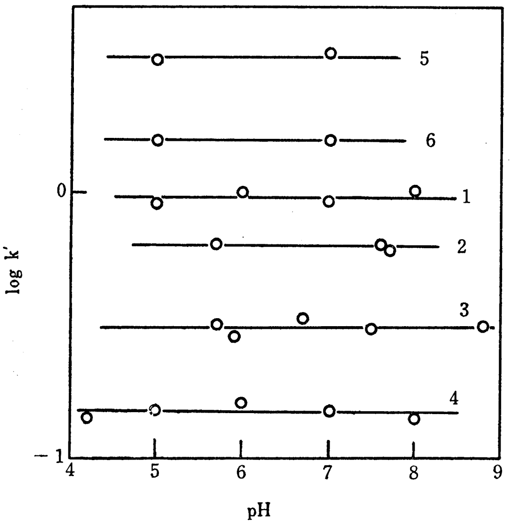


Fig. 5

Fig. 4. Effect of the concentration of iodide ion on the rate. Log k' versus log [I^-] plots at (1) 25°C (○), (2) 30°C (◐), and (3) 35°C (●).

Fig. 5. Relation between k' and the concentration of iodide ion. 1/k' versus [I^-] plots at (1) 25°C (○), (2) 30°C (◐), and (3) 35°C (●).



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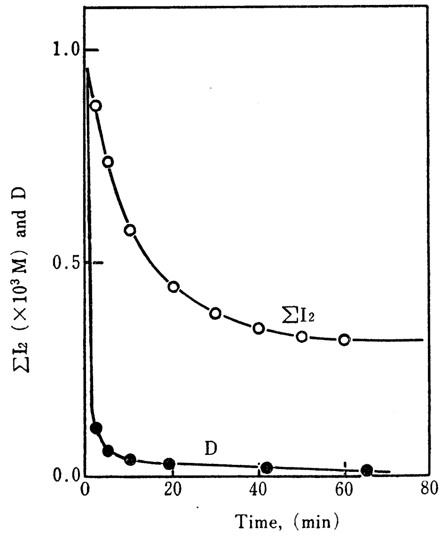


Fig. 7

Fig. 6. Effect of pH on the rate under the conditions of pH 4–9. Log k' versus pH plots. Temperature and concentration of iodide ion are (1) 25°C, 0.001 M, (2) 30°C, 0.008 M, (3) 30°C, 0.02 M, (4) 30°C, 0.03 M, (5) 35°C, 0.002 M, and (6) 35°C, 0.02 M.

Fig. 7. Comparison between the spectrophotometric method (●) and the back titration method (○) in alkaline aqueous solution. ΣI_2 or D versus time plots. Condition of reaction: 30°C, pH 12, KI 0.05 M, HCOONa 0.2 M,

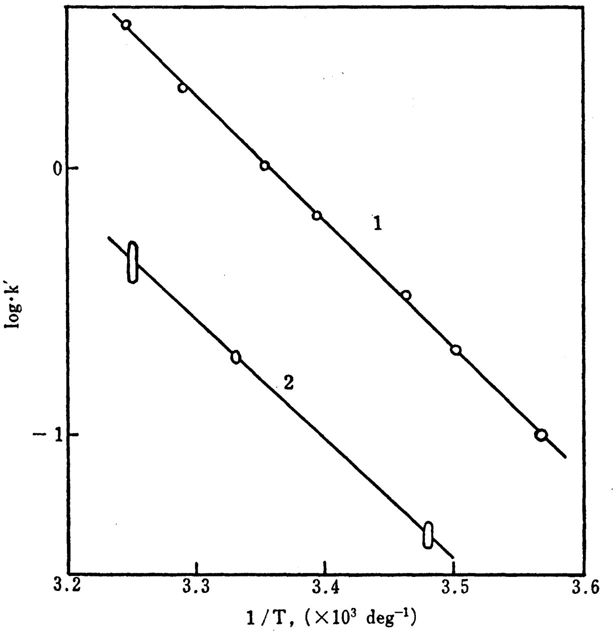


Fig. 8

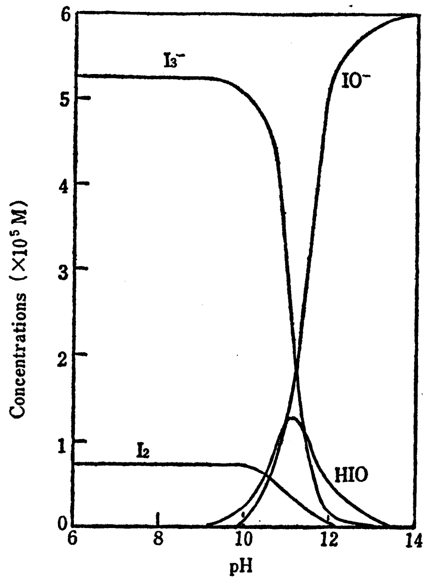


Fig. 9

Fig. 8. Arrhenius plots. (1) KI 0.002 M, HCOONa 0.01–0.06 M, Activation energy 21.3±0.1 kcal, (2) KI 0.02 M, HCOONa 0.39 M, Activation energy 20.7±0.5 kcal.

Fig. 9. Equilibrium diagram for $I_3^- \rightleftarrows I_2 + I^-$ (K_1), $I_2 + H_2O \rightleftarrows HIO + I^- + H^+$ (K_2) and $HIO \rightleftarrows H^+ + IO^-$ (K_3), where $K_1 = 1.36 \times 10^{-3}$, $K_2 = 3 \times 10^{-13}$, and $K_3 = 10^{-11}$. Initial concentration of iodide ion and iodine are 0.01 M and 6×10^{-5}M, respectively.

method and it contains I_3^-, I_2, IO^-, IO_3^-, etc. It is found that this reaction is the first order reaction about the total concentration of iodine. Similarly, this reaction is the first order reaction about the concentration of triiodide ion. The difference of the initial concentration of iodine have no effect toward the apparent first order rate constant, k_{obs} ($-d[\Sigma I_2]/dt = k_{obs}[\Sigma I_2]$, or $-dD/dt = k_{obs}D$, where D is an absorbance at 350 nm.). k_{obs} is the same between the back titration method and the spectrophotometric method when the other conditions are equal.

The effect of the concentration of formate ion is indicated in fig. 2 (the plot of log $[\Sigma I_2]$ or log D versus time). Increasing the concentration of formate ion, the rate constant k_{obs} increases. About these systems and the others, the plot of the logarithms of the concentration of formate ion versus the logarithms of k_{obs} is indicated in fig. 3. The gradiants are about one. It is found that this reaction is the first order reaction about the concentration of formate ion.

The effect of the concentration of iodide ion is studied. The plot of log k' ($k' = k_{obs}/[HCOO^-]$) versus log $[I^-]$ are indicated in fig. 4. It indicates that for the high concentration of iodide ion, the reaction is inversely proportional to the concentration of iodide ion, while for the low concentration of iodide ion, k' approaches constant. From these results, the next relation between k' and $[I^-]$ is assumed:

$$k' = a/([I^-] + b) \quad \text{or} \quad 1/k' = [I^-]/a + b/a$$

where a and b are constant. The plot of 1/k' versus $[I^-]$ is linear as shown in fig. 5,

TABLE 1. KINETIC DATA OF THE OXIDATION OF FORMATE IN TRIIODIDE AQUEOUS SOLUTION

(a) At 25°C (Spectrophotometric method)

pH	Concentration of			k_{obs} a) ($\times 10^2$min^{-1})	k' b) (M^{-1}min^{-1})
	Iodine ($\times 10^5$M)	Formate (M)	Iodide (M)		
7	9.23	0.014	0.0010	1.52	1.09
		0.025		2.65	1.06
		0.040		4.33	1.08
		0.060		6.75	1.125
		0.080		8.20	1.025
		0.10		9.28	0.928
		0.14		15.6	1.11
		0.20		19.6	0.981
		0.25		26.0	1.04
		0.30		28.1	0.937
6	3.94	0.10	0.0010	10.11	1.01
			0.0025	7.92	0.792
			0.0046	5.23	0.523
			0.0096	2.92	0.292
			0.0246	1.39	0.139
			0.0496	0.679	0.068
			0.100	0.329	0.033
			0.250	0.133	0.0133
			0.50	0.0667	0.0067
5	6.50	0.10	0.0010	13.8	1.38
	7.50		0.0014	12.9	1.29
	8.30		0.0016	12.0	1.20
	9.32		0.0020	10.6	1.06
	9.91		0.0022	9.90	0.99
	11.4		0.0026	8.94	0.89
	12.8		0.0030	8.01	0.80
5	9.23	0.10	0.001	9.19	0.92
6	3.94			10.11	1.01
7	9.23			9.28	0.93
8	9.23			10.16	1.02

a) $-dD/dt = k_{obs}\,D$, where D is the absorbance at 350 nm.
b) $k' = k_{obs}/[HCOO^-]$

(b) At 30°C (Back titration method)

pH	Concentration of			k_{obs} ($\times 10^2$min^{-1})	k' (M^{-1}min^{-1})
	Iodine ($\times 10^3$M)	Formate (M)	Iodide (M)		
6	0.468	0.129	0.030	2.17	0.168
	0.488			2.11	0.163
	0.790			1.99	0.154
	0.946			2.02	0.157
	2.15			2.11	0.163
	5.80			1.90	0.147
	6.40			1.81	0.140
6	∼1.0∼	0.07	0.030	1.21	0.172
		0.15		2.50	0.166
		0.20		3.38	0.169

Table 1. Continued

6	~1.0~	0.20	0.020	4.90	0.245
			0.040	2.63	0.132
			0.050	2.06	0.103
			0.060	1.82	0.091
			0.080	1.31	0.065
			0.090	1.16	0.058
			0.10	1.05	0.052
4.2	~1.0~	0.129	0.030	1.81	0.14
5				1.95	0.15
6				2.00	0.16
7				1.92	0.15
8				1.76	0.14
8.8	0.156	0.393	0.020	12.4	0.315c)
7.5				11.9	0.303c)
6.7				13.2	0.336c)
5.9				11.2	0.285c)
5.7				12.4	0.315c)
7.7	—	0.20	0.080	12.3	0.615c)
7.6	—			12.8	0.642c)
5.7	—			12.8	0.640c)

c) Spectrophotometric method

(c) At 35°C (Spectrophotometric method)

pH	Concentration of			k_{obs} ($\times 10^2 min^{-1}$)	k' ($M^{-1}min^{-1}$)
	Iodine ($\times 10^5 M$)	Formate (M)	Iodide (M)		
7	6.32	0.0040	0.0020	1.44	3.59
		0.0060		1.93	3.22
		0.0080		2.68	3.35
		0.010		3.29	3.29
		0.020		6.47	3.23
		0.060		19.8	3.29
		0.070		23.0	3.48
		0.080		23.9	2.99
7	4.73	0.009	0.010	0.97	1.08
		0.012		1.29	1.08
		0.040		4.33	1.08
		0.060		5.77	0.96
		0.10		10.9	1.09
7	—	0.050	0.0010	18.0	3.60
	—	0.010	0.0060	1.50	1.50
	—	0.060	0.0060	9.59	1.60
	—	0.010	0.020	0.60	0.60
	—	0.060	0.020	3.11	0.52
	—	0.012	0.040	0.33	0.28
	—	0.080	0.040	2.28	0.29
5	6.32	0.009	0.002	2.84	3.15
		0.012		3.71	3.09
		0.040		12.75	3.19
	7.03	0.060		17.7	2.95
		0.090		26.5	2.94
		0.17		51.8	3.05
5	—	0.050	0.0060	7.92	1.58
	—	0.060	0.010	5.79	0.97
	—	0.050	0.020	2.80	0.56
	—	0.060	0.040	1.76	0.29

TABLE 2. EFFECT OF TEMPERATURE ON THE RATE

Temperature (°C)	k' ($M^{-1}min^{-1}$)	Temperature (°C)	k' ($M^{-1}min^{-1}$)
7.0	0.101	14	0.046[c]
12.3	0.215	14	0.039[d]
15.6	0.328	27	0.196[c]
21.5	0.669	27	0.199[d]
25.0	1.022	35	0.504[c]
30.8	1.979	35	0.431[d]
35.0	3.404		

$E_a=21.3\pm0.1$ kcal[a] $E_a=40.7\pm0.5$ kcal[b]

a) $[I^-]$, 0.0020 M; $[HCOO^-]$, 0.60~0.010 M; $[I_2]_0$, 6.3×10^{-5} M; pH 7, Spectrophotometric method

b) $[I^-]$, 0.020 M; $[HCOO^-]$, 0.393 M; $[I_2]_0$, 1.6×10^{-4} M; Spectrophotometric method

c) pH 6

d) pH 7.5

TABLE 3. k AND b IN THE EQUATION (1): Rate=$k[I_3^-$ or $\Sigma I_2]$ $[HCOO^-]/([I^-]+b)$

Temperature (°C)	k ($\times10^2$ min^{-1})	b ($\times10^3$M)
25	0.334	1.19
30	0.536	1.71
35	1.21	1.84

The effect of pH on the rate constant is indicated in fig. 6. It indicates that the change of pH has no effect under a condition of pH 4–9.

At high pH (above 11), a disproportionation of iodine arises. At high pH, the plot of the absorbance at 350 nm versus time dose not agree with that of the total concentration of iodine versus time (fig. 7). The hypoiodide ion, the iodite ion, and the iodate ion are formed by the disproportionation of iodine and these are titrated by thiosulfate ion. Accordingly, ΣI_2 is a summation of I_2, I_3^-, IO^-, IO_2^-, IO_3^-, etc. The disproportionation of iodine has no change of ΣI_2. But the absorbance at 350 nm results from the triiodide ion primarily. Therefore, the absorbance at 350 nm decreases both with the propagation of the disproportionation and with the propagation of the oxidation reaction of formate. Accordingly, the back titration method measures only the oxidation reaction of formate, while the spectrophotometric method measures both reactions: the disproportionation and the oxidation reaction of formate.

From all the results given above, the rate equation is written as follows:

$$\begin{aligned} -d[\Sigma I_2]/dt &= k[\Sigma I_2]\,[HCOO^-]/([I^-]+b) \\ -d[I_3^-]/dt &= k[I_3^-]\,[HCOO^-]/([I^-]+b) \end{aligned} \qquad (1)$$

The condition of reaction, k_{obs}, and k' are summarized in table 1. k and b in eq. (1) are given in table 3.

The higher the temperature, the faster the reaction rate is. The Arrhenius plot is given in fig. 8 and the data are given in table 2. The activity energy is 21 kcal.

Discussion

It has been thought that the source of the oxidizing effect of formate is molecular iodine, hypoiodous acid, or atomic iodine. If the iodine atom is the oxidizing species, the next mechanism and the rate equation are considered[5),6)]:

$$I_3^- \rightleftarrows I_2 + I^- \tag{2}$$

$$I_2 \rightleftarrows 2I \tag{3}$$

$$I + HCOO^- \rightarrow HCOOI^- \tag{4}$$

$$HCOOI^- + I_2 \rightarrow CO_2 + 2I^- + I + H^+ \tag{5}$$

By applying the steady state treatment to iodine atom,

$$-d[HCOO^-]/dt = k_{1/2}[HCOO^-]\sqrt{K_0K_1[\Sigma I_2]/(K_1+[I^-])} \tag{6}$$

where K_0 is the equilibrium constant for the reaction (3), K_1 is the equilibrium constant for the reaction (2), and $k_{1/2}$ is the rate constant for the reaction (4). The reactions (4) and (5) are the chain propagating reactions. This rate equation does not agree with the experimental equation (1).

When the hypoiodous acid oxidates the formate ion, the mechanism and the rate equation are considered as follows:

$$I_3^- \rightleftarrows I_2 + I^- \tag{7}$$

$$I_2 + H_2O \rightleftarrows HIO + H^+ + I^- \tag{8}$$

$$HIO + HCOO^- \rightarrow \text{Products} \tag{9}$$

Assuming that the reaction (9) is the rate determining step and applying the preliminary equilibrium treatment to the reaction (7) and (8),

$$-d[I_3^-]/dt = k_3K_1K_2[HCOO^-][I_3^-]/(K_1K_2 + K_1[H^+][I^-] + [H^+][I^-]^2) \tag{10}$$

where K_2 is the equilibrium constant for the reaction (8), and k_3 is the rate constant for the reaction (9). Since $K_1 = 1.36 \times 10^{-3}$, $K_2 = 3 \times 10^{-13}$ at 25°C[11),12)], and $[I^-] = 10^{-3}$ M, the effect of pH on the rate is greater between pH 5 and 9. This is inconsistent with the experimental facts. It was proposed that in the thermal oxidation of oxalates by bromine[13)] and chlorine[14)], the determining step is a reaction between the $HC_2O_4^-$ ion and the hypoiodous acid HOX formed by hydrolysis of the halogene and the rate equation is

$$\text{rate} = k[HC_2O_4^-]\,[\Sigma X_2]/(K_1 + [X^-])\,[X^-]\,[H^+] \tag{11}$$

where K_1 is the equilibrium constant for $X_3^- \rightleftarrows X_2 + X^-$, and $[\Sigma X_2]$ is the total concentration of halogene determined by titration. This rate equation has no analogy with the rate equation (1).

According to an equilibrium diagram (fig. 9), which is calculated by the next equilibriums and equilibrium constant:

$$I_3^- \rightleftarrows I_2 + I^- \qquad K_1 = 1.36 \times 10^{-3}$$

$$I_2 + H_2O \rightleftarrows HIO + H^+ + I^- \qquad K_2 = 3 \times 10^{-13}$$

$$HIO \rightleftarrows H^+ + IO^- \qquad K_3 = 10^{-11}\ {}^{15)}$$

the concentration of hypoiodous acid is very small in comparison with the concentration of triiodide ion and iodine molecule below pH 9. It is necessary for studying the effect of hypoiodous acid that the experiments are done under the condition of high pH.

When the oxidizing species is the iodine molecule, the next mechanism and the rate equation are considered:

$$I_3^- \rightleftarrows I_2 + I^- \qquad K_1 \qquad (12)$$

$$I_2 + HCOO^- \rightarrow \text{Products} \qquad k_2 \qquad (13)$$

Assuming that the reaction (13) is the rate determining step, and applying the preliminary equilibrium treatment to the reaction (12),

$$\left.\begin{aligned} -d[I_3^-]/dt &= k_2K_1[I_3^-]\,[HCOO^-]/(K_1+[I^-]) \\ -d[\Sigma I_2]/dt &= k_2K_1[\Sigma I_2]\,[HCOO^-]/(K_1+[I^-]) \end{aligned}\right. \qquad (14)$$

This rate equation has a good agreement with both the results from the spectrophotometric method and the back titration method. Also, b in eq. (1) is a good agreement with $K_1(\approx 10^{-3})$.

In the reaction between formic acid and thallium (III) in aqueous solution, the decomposition of the intermediate $Tl \cdot HCOOH^{3+}$ has the activation energy of 26.6 kcal[16]. Then, the mechanism of the reaction between formate and iodine is also assumed as follows:

$$HCOO^- + I_2 \rightleftarrows HCOO^- \cdot I_2 \qquad K_2 \qquad (15)$$

$$HCOO^- \cdot I_2^+ \rightarrow H + CO_2 + 2I^- \qquad k_3 \qquad (16)$$

The rate equation is

$$-d[I_3^-]/dt = k_3K_1K_2[HCOO^-]\,[I_3^-]/\{[I^-]+K_1(1+K_2[HCOO^-])\} \qquad (17)$$

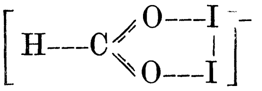
If $K_2[HCOO^-] \ll 1$, this rate equation is consistent with the equation (14). In this case, $k_2 = k_3K_2$. The reaction (16) has an activation energy of 21 kcal.

HILLER AND KRUEGER reported[9] that the reaction with $HCOO^-$ is faster than that with $DCOO^-$ ($k_H/k_D = 3.8$ in aqueous solution). They proposed that for the mechanism of the reaction between formate and iodine,

$$I_2 + HCOO^- \longrightarrow I_2H^- + CO_2 \qquad \text{(slow)}$$

$$I_2H^- \rightarrow 2I^- + H^+ \qquad \text{(fast)}$$

In this case, the activation complex is thought to be the three center bond complex ($[I_2—H—COO]^-$). From the isotope effect, this mechanism is probable. But the electron transfer is thought to be difficult. Then, we assumed that the activation complex is



The sp^2 hybridized orbital of carbon atom proceeds to the sp hybridized orbital and it cuts off proton and transfers electrons to iodine atoms. The isotope effect is explained that the C-D bond is difficult to cut off because the C-D bond is stronger than the C-H bond. This is supported by the fact that for the thallium (III) oxidation of formate $k_H/k_D=3.4$, a process which undoubtedly occurs *via* interaction of Tl^{3+} on the oxigen atom of formate[17]. But, it is difficult from ouly these results to rule out the possibility given by Hiller and Krueger.

Conclusion

By the kinetic study of the oxidation reaction of formate ion in an aqueous solution, the rate equation was obtained, that is, rate$=k[I_3^-][HCOO^-]/([I^-]+K_1)$. The change of pH has no effect on the rate under the condition of pH 4–9. It may be considered that the oxidizing species is the iodine molecule and the intermediate complex is $HCOO^-.I_2$ or I_2H^-.

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References

1) N. Dhar, *J. Chem. Soc.*, **111**, 707 (1917)
2) S.S. Doosay and W.V. Bhagwat, *Z. Anorg. Allg. Chem.*, **216**, 241 (1934)
3) O.G. Ingles and C.G. Israel, *J. Chem. Soc.*, **1948**, 810; **1949**, 1213
4) S. Nakamura, *Sci. Rep. Kagoshima Univ.*, **3**, 41 (1954); **4**, 1 (1955)
5) R.O. Griffith and A. Mckeown, *Trans. Faraday Soc.*, **28**, 752 (1932)
6) E. Abel and K. Hilferding, *Z. Phys. Chem.*, **A 172**, 353 (1935)
7) B.F. Chow, *J. Amer. Chem. Soc.*, **57**, 1437 (1935)
8) D.L. Hammick and M. Zverintzov, *J. Chem. Soc.*, **1926**, 1105
9) W. Hiller and J.H. Krueger, *Inorg. Chem.*, **6**, 528 (1967)
10) R.O. Griffith, A. Mckeown and A.G. Winn, *Trans. Faraday Soc.*, **29**, 369 (1933)
11) Jakowkin, *Z. Phys. Chem.*, **13**, 539 (1894); **20**, 19 (1896); Bray and Mckay, *J. Amer. Chem. Soc.*, **32**, 914, 1207 (1910)
12) Bray, *J. Amer. Chem. Soc.*, **33**, 932 (1911)
13) R.O. Griffith, A. Mckeown, and A.G. Winn, *Trans. Faraday Soc.*, **28**, 107 (1932)
14) R.O. Griffith and A. Mckeown, *ibid.*, **28**, 518, 616 (1932)
15) Furth, *Z. Electrochem.*, **28**, 57 (1922)
16) H.N. Halvorson and J. Halpern, *J. Amer. Chem. Soc.*, **78**, 5562 (1956)
17) J. Halpern and S.M. Taylor, *Discuss. Faraday Soc.*, **29**, 174 (1960)