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The Oxidation of Sodium Formate with Iodine. II. The Kinetics on the Reaction in an Ethanol Solution

By

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The kinetics of the oxidation of sodium formate with iodine was studied in an ethanol solution. The rate equation was obtained as follows: $-d[I_2]/dt=k''[I_2]\,[HCOONa]/([KI]+a)$, where $k''=0.020$ min^{-1} and $a=1.26\times10^{-4}$ M were obtained as 34.6°C. This rate equation suggested that the reaction between an iodine molecule and a formate ion was the rate determining step. The possible mechanism was given. The equilibrium constant of the reaction, $I_3^- \rightleftarrows I_2+I^-$, in an ethanol solution was obtained to be 0.6×10^{-4} M at the room temperature by the spectrophotometric measurements and it was comparable to that obtained by the rate equation (1.26×10^{-4} M at 34.6°C) within a usual error by the kinetic measurements.

The kinetic studies of the oxidation of sodium formate with iodine in an aqueous solution clarified that the reaction between an iodine molecule and a formate ion was a rate determining step.[1] Hiller and Krueger found that the reaction was significantly accelerated by the increase of dimethylsulfoxide in the binary solvent of water and dimethylsulfoxide.[2] During the course of an investigation of the kinetics of the reaction in the binary solvent of water and alcohol,[3] it became desirable to clarify the mechanism of the reaction in an alcohol solution.

This work was undertaken to determine the rate equation of the reaction and to obtain the information of the mechanism of the reaction. The equilibrium between iodine and triiodide was also discussed on the basis of the spectrophotometric measurements in an ethanol solution.

Experimental

Materials. Iodine, potassium iodide, and sodium formate (all GR) were obtained commercially. Iodine was purified by sublimation of a mixture of iodine and potassium iodide.[4] The purified iodine was dried for a day in a desiccator and was used. The iodine solution was prepared by dissolving a weighed quantity of the purified iodine in ethanol. Potassium iodide and sodium formate were used after drying at 120 °C for 12 hours. Ethanol (Super special grade) obtained from Wako Junyaku Co. was used without

further purification.

Measurements. Spectra were measured using a Shimadzu SV-50 spectrophotometer. The reaction was followed by measuring the optical density at 360 nm using a Hitachi 101 spectrophotometer with a thermostated optical cell (10 mm). The optical density at 360 nm was proportional to the concentration of iodine in the presence of 5 mM potassium iodide. In all kinetic runs, potassium iodide and sodium formate were present in excess sufficient to eliminate a perturbation due to the iodide ion produced and the formate ion decomposed during the reaction.

Results and Discussions

Spectra of the Ethanol Solution of Iodine. The ethanol solution of various concentrations of iodine gives the spectra as shown in Fig. 1 in the presence of 5 mM KI. The peak of iodine molecule at 447 nm was not observed. The optical density at 360 nm, D_{360}, is proportional to the concentration of iodine as shown in Fig. 2.

The optical density at 360 nm increased with the increase in potassium iodide at a constant concentration of iodine, but it was not proportional to the concentration of the iodide. Assuming that the increase in D_{360} with the iodide is owed to the following equilibrium,

$$I_2 + I^- \rightleftarrows I_3^- , \tag{1}$$

the apparent molar extinction coefficient of the solution, $\bar{\varepsilon}$, is given by Eq. (2):

$$\begin{aligned} \bar{\varepsilon} &= D_{360}/C_{I_2} = (\varepsilon_0 + \varepsilon_1 K_1 C_{I^-})/(1 + K_1 C_{I^-}) \\ &= \varepsilon_1 + (\varepsilon_0 - \varepsilon_1)/(1 + K_1 C_{I^-}) , \end{aligned} \tag{2}$$

where ε_0 and ε_1 are the molar extinction coefficients of the iodine molecule and the triiodide

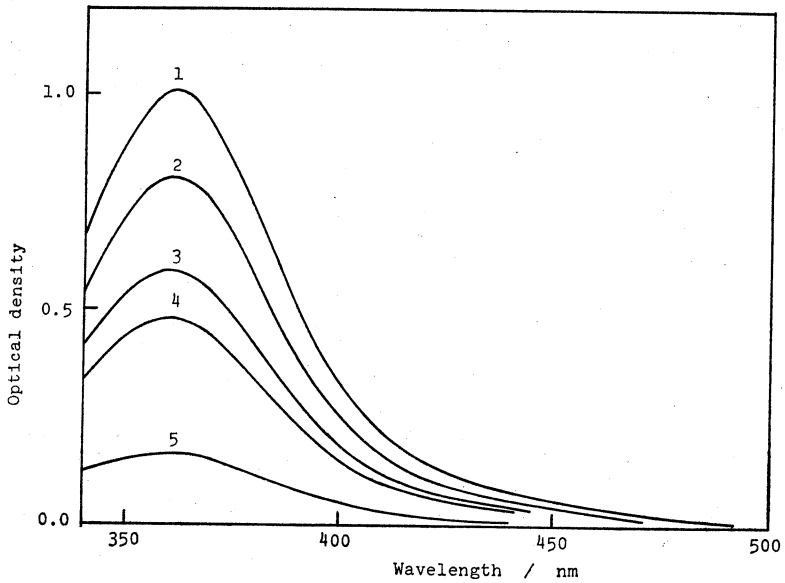

Fig. 1. Absorption spectra of the ethanol solution of iodine with 5.2 mM KI. Iodine: 1. 4.5, 2. 3.5, 3. 2.5, 4. 2.0, 5. 0.8×10^{-5} M.

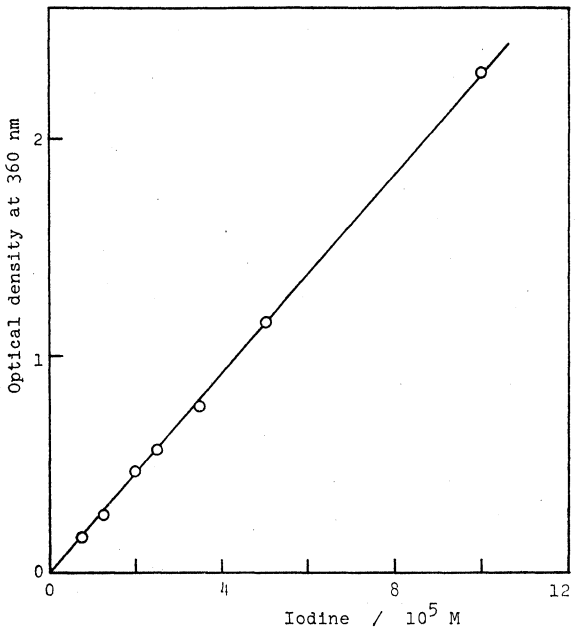

Fig. 2. Dependence of the optical density at 360 nm on the concentration of iodine with 5.2 mM KI at the room temperature.

ion respectively, C_{I_2} and C_{I^-} are the gross concentration of iodine and iodide respectively, and K_1 is the equilibrium constant of the reaction (1). On the basis of Eq. (2), the normalized curves of $y=p/(1+x)$, which are the plots of y *vs.* log x, could be plotted with various values of p. When the plot of $\bar{\varepsilon}$ *vs.* log C_{-I} was compared with the normalized curves, the values of K_1, ε_0, and ε_1 could be obtained to be 1.67×10^4 M^{-1}, 0.34×10^4 $M^{-1}cm^{-1}$, and 1.94×10^4 $M^{-1}cm^{-1}$ respectively at the room temperature (The curve-fitting method[5,6]). The experimental data of $\bar{\varepsilon}$ agree with the curve calculated by use of the values of K_1, ε_0, and ε_1 as shown in Fig. 3. The agreement proved that the increase in D_{360} with the iodide was based on the increase of triiodide ion.

Kinetics. When the ethanol solution of the mixture of iodine and potassium iodide was stand for 25 hours, the optical density of the solution increased only a little intensity (below 0.05 O.D.). The change was too late to compare the rate of the reaction of iodine with sodium formate and its effect could be neglected.

As a plot of log D_{360} *vs.* time gave a straight line, it was found that the reaction was the first-order reaction in iodine. The apparent first-order rate constants, k', are given in Table 1 at various concentrations of iodine. That the rate constant was independent on the initial concentration of iodine supported that the reaction was the first-order reaction in iodine.

At various concentrations of sodium formate, good first-order rate plots were obtained. At the low concentration of the formate below 0.5 mM, the plots, however, curved in the final step of the reaction. It was considered to be owed to the decrease of the formate by the reaction. The apparent first-order rate constants are given in Table 2. As a plot of log k' *vs.* log [HCOONa] gives a straight line with a slope of 1 as shown in Fig. 4, the

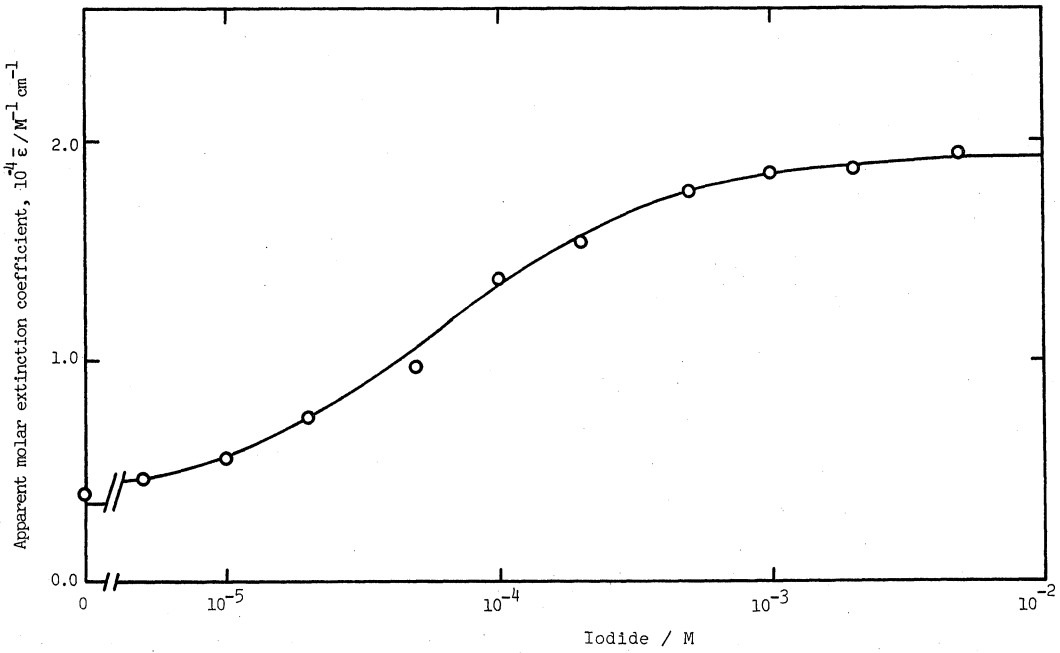

Fig. 3. Plot of the apparent extinction coefficient *vs.* log [KI]. The solid line is the cruve calculated by use of the values of $K_1=1.67\times10^{-4}$ M, $\varepsilon_0=0.34\times10^4$ $M^{-1}cm^{-1}$, and $\varepsilon_0-\varepsilon_1=-1.6\times10^4$ $M^{-1}cm^{-1}$ in Eq. (2).

TABLE 1. THE APPARENT FIRST-ORDER RATE CONSTANTS AT VARIOUS CONCENTRATIONS OF IODINE

(Sodium formate was 5 mM with 5 mM KI at 34.6°C)

Iodine (10^5 M)	Rate constant (10^3 min^{-1})
10	18.9
7.0	20.0
5.0	20.4
2.0	19.6

TABLE 2. THE APPARENT FIRST-ORDER RATE CONSTANTS AT VARIOUS CONCENTRATIONS OF SODIUM FORMATE

(Iodine was 0.05 mM with 5 mM KI at 34.6°C)

Formate (mM)	Rate constant (10^3 min^{-1})
6.0	21.3
5.0	19.7
4.0	15.4
2.0	7.81
1.0	3.64
0.5	2.00
0.2	0.79

reaction was found to be the first-order reaction in formate.

At various concentrations of potassium iodide above 0.2 mM, good first-order rate plots were obtained. A plot of log k' *vs.* log [KI] is shown in Fg. 5. At the high concentration of the iodide above 1 mM, the plot gave a straight line with a slope of -1, but the plot curved at the lower concentration of the iodide. From this result, the relationship

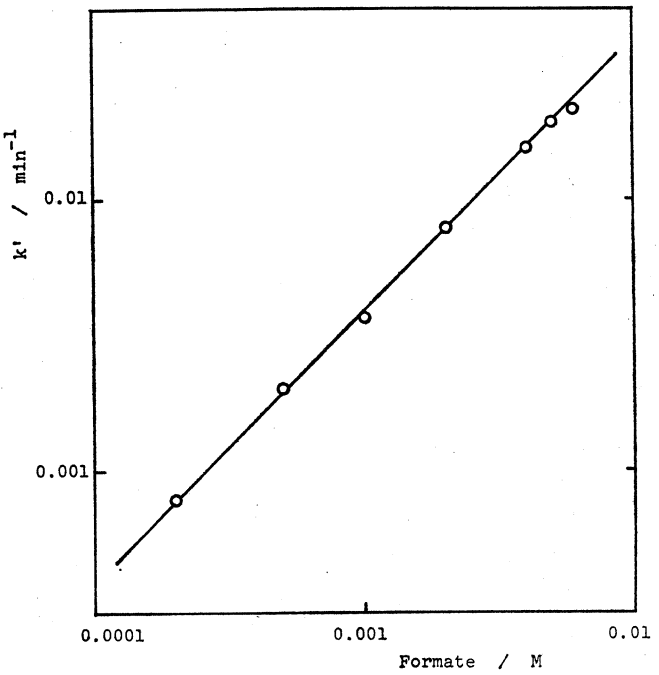

Fig. 4. Dependence of the apparent first-order rate constant on the concentration of sodium formate with *ca.* 5×10^{-5} M I_2 and 5 mM KI at 34.6 °C.

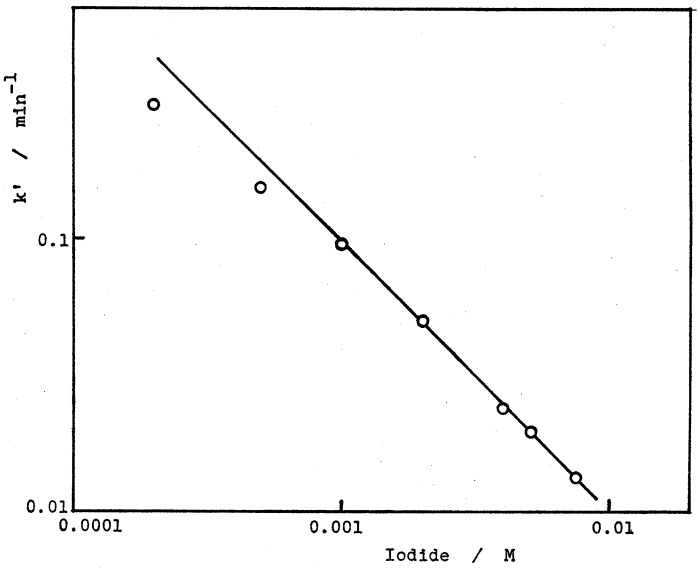

Fig. 5. Dependence of the apparent first-order rate constant on the concentration of potassium iodide with *ca.* 5×10^{-5} M I_2 and 5 mM HCOONa at 34.6 °C. The solid line is the straight line with a slope of –1.

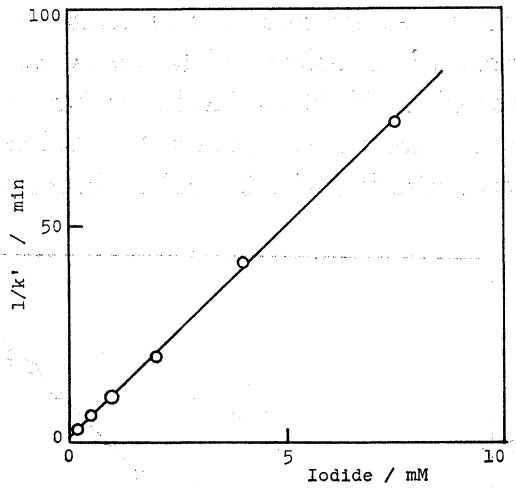

Fig. 6. Dependence of the reciprocal of the rate constant on the concentration of the iodide with *ca.* 5×10^{-5} M I_2 and 5 mM HCOONa at 34.6 °C. The solid line is indicated by the equation $1/k'=9.76\times10^{3}[I^-]+1.23$.

represented by Eq. (3) was assumed:

$$k' = b/([KI]+a) \quad \text{or} \quad 1/k' = [KI]/b+a/b\,, \tag{3}$$

where a and b are constant. The plot of $1/k'$ *vs.* [KI] gives a straight line as shown in Fig. 6. The constants, a and b, were obtained to be 1.26×10^{-4} M and 1.02×10^{-4} M min^{-1} respectively.

From the previous results, the rate equation was obtained as follows:

$$-d[I_2]/dt = k''[I_2][HCOONa]/([KI]+a)\,, \tag{4}$$

where $k''=0.020$ min^{-1} and $a=1.26\times10^{-4}$ M.

On the basis of this rate equation, the following mechanism was proposed in analogy with the reaction in an aqueous solution:[1)]

$$I_3^- \rightleftarrows I_2+I^- \qquad K_{-1} \tag{5}$$

$$I_2+HCOO^- \rightarrow CO_2+HI+I^- \qquad k \tag{6}$$

Assuming that the reaction (6) is the rate determining step and applying the preliminary equilibrium treatment to the reaction (5), the following rate equation is obtained:

$$-d[I_2]/dt = kK_{-1}[I_2]\,[HCOO^-]/([I^-]+K_{-1}) \tag{7}$$

where K_{-1} is the equilibrium constant of the reaction (5) and it equals to $1/K$. The comparison of Eq. (7) with Eq. (4) indicated that $K_{-1}=1.26\times10^{-4}$ M ($K_1=0.79\times10^{4}$ M^{-1}).

The equilibrium constant of the reaction (1) obtained by the spectrophotometric measurements (1.67×10^{4} M^{-1}) is larger by a factor of 2 than that obtained by the kinetic measurements, but the difference is within the usual difference by the kinetic measurements. This fact supported the mechanism supposed in Eqs. (5) and (6).

The rate constant of the reaction (6) and the equilibrium constant of the reaction (5), k and K_{-1}, are compared with those obtained in an aqueous solution in Table 4. The

Table 3. The apparent first-order rate constants at various concentrations of potassium iodide
(Iodine was 0.05 mM with 5 mM HCOONa at 34.6°C)

Iodide (mM)	Rate constant (10^3 min^{-1})
7.5	13.5
5.0	20.4
4.0	24.1
2.0	50.0
1.0	95.2
0.50	154
0.20	312

Table 4. The kinetic parameters

	k ($M^{-1}min^{-1}$)	K_{-1} (M)	Temperature (°C)
in ethanol solution	160	1.26×10^{-4}	34.6
in aqueous solution	6.6	1.84×10^{-3}	35

rate constant is much larger in an ethanol solution than in an aqueous solution. This difference may be based on the difference of solvation. The effect of the solvation on the rate was studied using a binary solvent mixture of water and alcohol. The details will be reported elsewhere.

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3) It will be reported elsewhere.
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