July, 1977] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (7), 1767—1770 (1977) 1767

Kinetics of the Oxidation of Formate by Iodine in the Water–Methanol and the Water–Ethanol Mixed Solvents

Katumitu HAYAKAWA and Makoto SATO
Department of Chemistry, Faculty of Science, Kagoshima University, Koorimoto, Kagoshima 890

(Received December 9, 1976)

The kinetics of the iodine–formate reaction gives an identical rate equation in several water–alcohol mixed solvents: rate=k[HCOO$^-$] [I$_3^-$]/(a[I$^-$]+1). The values of k/M^{-1} s^{-1} and 10^{-3} a/M^{-1} are 5.5 and 16 in ethanol at 35 °C, 3.6 and 12 in methanol at 30 °C, and 0.06 and 0.7 in water at 30 °C, respectively. The values of a are comparable to the formation constants of I$_3^-$ in the water–alcohol mixtures. The rate-determining step is the reaction between an iodine molecule and a formate ion. The activation parameters, ΔH^*/kJ mol^{-1} and ΔS^*/J K^{-1} mol^{-1}, are 71 and −1 in the 0.95 mole fraction of methanol, 60 and −32 in the 0.92 mole fraction of ethanol, and 75 and −20 in water, respectively. The entropy term contributes to the acceleration by alcohol in the water–methanol mixtures, whereas both the entropy term and the enthalpy term contribute to the acceleration in the water–ethanol mixtures. These effects of the mixed solvents suggest that the specific interactions of the solvent molecule with the reactants and the activated complex, such as a specific solvation or a hydrogen bond, play an important role in the rate-determining step.

The iodine–formate reaction 1 is remarkably accelerated by the addition of dimetyl sulfoxide(DMSO) to water:[1)]

$$I_3^- + HCOO^- \longrightarrow 3I^- + H^+ + CO_2 \qquad (1)$$

According to the electron-transfer theory,[2)] changes in dielectric properties are expected to affect the reorganization of a solvent molecule around the reactants and the activated complex. The water–alcohol solvent mixtures exhibit pronounced structural and dielectric changes at different component ratios.[3)] In the present paper, we will deal with the kinetics of Reaction 1 and will determine the activation parameters in the water–methanol and water–ethanol mixed solvents. The dependence of the rate and the activation parameters on the changes in such bulk properties as the dielectric property will be discussed quantitatively. The changes in the microscopic properties around the reactants and the activated complex, such as the specific solvation or the hydrogen bond, play an important role in the rate-determining step in Reaction 1.

Experimental

Reagents. The iodine, potassium iodide, sodium formate, methanol, and ethanol were obtained commercially. The ethanol was of Wako's super special grade, while the other substances were of a guaranteed grade. The iodine was purified by sublimation, and the solutions were prepared by dissolving the iodine in the potassium iodide solution in each measurement. The potassium iodide and sodium formate were dried at 120 °C overnight. The sodium perchlorate was obtained from BDH Chemicals, Ltd. It was recrystallized from water and used as a control of the ionic strength of the solutions. The pH of the aqueous solution was controlled using a phosphate buffer. In the water-alcohol mixed solvents, the pH and ionic strength of the solution were uncontrolled.

Measurements. The reaction was followed by measuring the absorbance at 350 nm at different times, using a Hitachi 101 spectrophotometer with quartz cells in a thermostated holder. When high iodide concentrations are employed, the iodine is completely converted into the triiodide ion. The ion is the only species which absorbs appreciably at 350 nm. Independent experiments showed that Beer's law was obeyed in water–alcohol mixed solvents. The reaction was also followed by measuring the concentration of total iodine in the aqueous solution by iodometry. Both methods give the same rate constant.

When mixtures of iodine and potassium iodide in several mixed solvents were left standing for 25 h, the absorbance of the solutions changed slightly (below 5%). The change was neglected compared with the rate of the reaction of iodine with formate. Irradiation with light of 350 nm had no effect on the rate.

Results and Discussion

Kinetics and the Mechanism. The rate depended on the concentrations of iodine, iodide, and formate, and in the aqueous solution it was independent of the pH at 4—9 and of the ionic strength below 0.6 M, as is shown in Table 1.

In all the kinetic runs, the initial concentrations of iodide and of formate were chosen to be much greater than the initial total iodine concentration. Under these conditions, the reaction was found to be a first-order reaction of the triiodide ion. The apparent first-order rate constant, k_{app}, is proportional to the formate concentration (Fig. 1). Figure 2 shows that the plot of $1/k'$ *vs.* [I$^-$], where $k'=k_{\mathrm{app}}$/[HCOO$^-$], gives a straight line with an intercept. Thus, the following rate law describes the kinetics in the present solvents:

$$\text{Rate} = -\mathrm{d}[I_3^-]/\mathrm{d}t = k[I_3^-][HCOO^-]/(a[I^-]+1). \qquad (2)$$

Table 2 shows the kinetic parameters, k and a, in the various solvents.

TABLE 1. THE EFFECTS OF THE pH AND THE IONIC STRENGTH ON THE RATE IN AN AQUEOUS SOLUTION AT 30 °C

pH	$10^3\,k_{\mathrm{app}}$/s^{-1}	I_c	$10^4\,k_{\mathrm{app}}$/s^{-1}
8.8	2.1	0.035	0.77
7.5	2.0	0.055	0.81
6.7	2.2	0.085	0.85
5.9	1.9	0.12	0.84
5.7	2.1	0.32	0.74
[HCOONa]/M=0.39		0.62	0.81
[KI]/M=0.015		[HCOONa]/M=0.02	
		[KI]/M=0.02	

TABLE 2. THE KINETIC PARAMETERS IN VARIOUS SOLVENTS

Solvent	$k/\mathrm{M}^{-1}\,\mathrm{s}^{-1}$	$10^{-3}\,a/\mathrm{M}^{-1}$	$10^{-3}\,K_f/\mathrm{M}^{-1}$	t/°C
EtOH(0.98)	5.5±0.1	16±1	17	35
$EtOH-H_2O$(0.24)	1.1±0.6	7±4	7.6	30
H_2O(0.00)	0.11±0.01	0.57±0.03	0.59	35
H_2O(0.00)	0.06±0.02	0.7±0.2	0.66	30
$MeOH-H_2O$(0.31)	0.37±0.08	2.3±0.4	2.7	30
MeOH(0.99)	3.6±1.0	12±3	11	30

( ): mole fraction of alcohol.

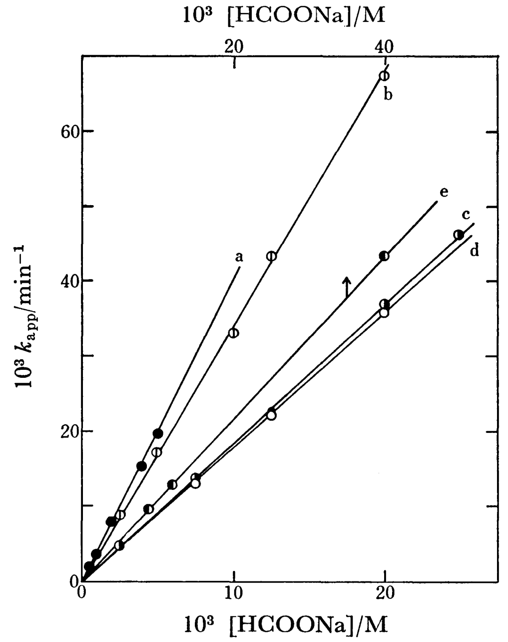


Fig. 1. Dependence of the apparent first-order rate constant on the formate concentration in various solvents: a. EtOH, b. MeOH, c. $EtOH-H_2O$, d. $MeOH-H_2O$, e. H_2O.

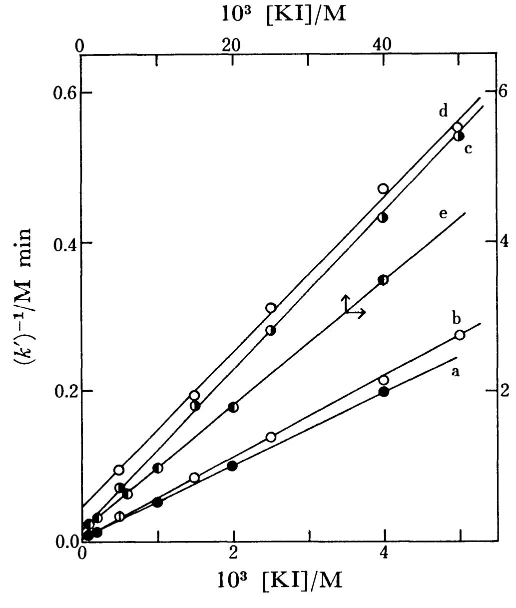


Fig. 2. Dependence of $k'(=k_{app}/[HCOO^-])$ on the iodide concentration in various solvents: a. EtOH, b. MeOH, c. $EtOH-H_2O$, d. $MeOH-H_2O$, e. H_2O.

The rate equation is derived from the following mechanism:[1]

$$I_3^- \underset{k_{3-}}{\overset{k_{3+}}{\rightleftharpoons}} I_2 + I^-, \tag{3}$$

$$I_2 + HCOO^- \xrightarrow{k_4} \text{Products}. \tag{4}$$

When k_4, k_{3+}, and k_{3-} are the rate constants of the respective reactions,

$$-d[I_2]/dt = k_4[I_2][HCOO^-] - k_{3+}[I_3^-] + k_{3-}[I_2][I^-], \tag{5}$$

$$\begin{aligned}-d[I_3^-]/dt &= k_{3+}[I_3^-] - k_{3-}[I_2][I^-]\\ &= d[I_2]/dt + k_4[I_2][HCOO^-].\end{aligned} \tag{6}$$

Assuming that Reaction 4 is slow and Reaction 3 is in pseudo-equilibrium,

$$[I_2] = [I_3^-]/(K_f[I^-]), \tag{7}$$

where K_f is the formation constant of I_3^-.

$$\begin{aligned}\frac{d[I_2]}{dt} &= \frac{1}{K_f[I^-]}\left(\frac{d[I_3^-]}{dt} - \frac{[I_3^-]}{[I^-]}\frac{d[I^-]}{dt}\right)\\ &\approx \frac{1}{K_f[I^-]}\frac{d[I_3^-]}{dt},\end{aligned} \tag{8}$$

because $[I_3^-]/[I^-] \ll 1$ and $|d[I^-]/dt| \leqslant |3d[I_3^-]/dt|$. When Eqs. 7 and 8 are substituted into Eq. 6,

$$-d[I_3^-]/dt = k_4[I_3^-][HCOO^-]/(K_f[I^-]+1). \tag{9}$$

Thus, the experimental kinetic parameters, k and a, equal k_4 and K_f respectively. The fourth column in Table 2 shows the K_f values obtained by the spectrophotometric method.[4] The finding that K_f is comparable to a supports the mechanism proposed in the present study. The mechanism involving the iodine atom[5,6] is eliminated because the rate must be proportional to the root of the iodine concentration in the mechanism. The effects of the pH and the water content of the solvent on the rate eliminate the mechanism involving hypoiodous acid.[7] The fact that the rate was independent of the ionic strength of the solution indicates that the rate-determining step involves a non-ionic species[8-12] and supports the mechanism proposed in the present study.

The slow step involves an iodine attack on the formate anion, although one can only speculate about the nature of the following intermediate. Hiller and Krueger[1] proposed a rate-determining step involving a transfer of a hydride ion from carbon to iodine, as is shown in Eq. 10, because $DCOO^-$ has a considerable effect on the rate ($k(HCOO^-)/k(DCOO^-)=3.8$ in water and 2.2 in DMSO).

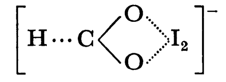
$$I_2 + HCOO^- \longrightarrow I_2H^- + CO_2 \quad \text{(slow)}, \tag{10}$$

$$I_2H^- \longrightarrow 2I^- + H^+ \quad \text{(fast)}. \qquad (11)$$

In order to estimate the srtucture of the activated complex, the MO's energy and the formal charge for $HCOO^-$ were calculated by means of the CNDO method. The calculation indicated that the energy level of the highest occupied orbital of $HCOO^-$ (-2.26 eV) is higher than that of the lowest vacant orbital in I_2 (-7.0 eV[13]). It seems that the iodine molecule is an electrophilic reagent in the reaction with the formate ion.[14] The formal charge and the frontier electron density[15] of $HCOO^-$ shown in Table 3 suggest that an iodine molecule attacks the O-atom in $HCOO^-$. The kinetic isotope data[1] suggest that the H–C bond is loosened or severed by the attack of the iodine molecule. Thus, the activated complex may be proposed to be **1**, in which the C–H bond is greater than those in a formate ion.

TABLE 3. THE FORMAL CHARGE AND THE FRONTIER ELECTRON DENSITY IN THE $HCOO^-$ ION

Atom	Formal charge	Frontier electron density
H	+0.20	0.0
C	−0.27	0.0
O	−0.47	1.0



1

Table 2 shows that the rate in alcohol is much faster than that in water. The dependence of the rate on the solvents is, clearly, not caused by the change in the mechanism in the water–alcohol mixed solvents.

The Activation Parameters in the Mixed Solvents. The apparent first-order rate constants were determined at various temperatures in mixed solvents of various alcohol contents. The rate constant, k, was calculated using the formation constant of the triiodide ion, K_f, which was determined by the spectrophotometric method.[4] Table 4 shows the values of k, ΔH^*, ΔS^*, and the relative thermodynamic functions of activation, $\Delta(\Delta H^*)$ and $\Delta(-T\Delta S^*)$. The small maximum in ΔH^* appears near the 0.1 mole fraction of methanol, and the entropy term contributes to the acceleration by alcohol in the water–methanol system, whereas the maximum in ΔH^* disappears and both the entropy term and the enthalpy term contribute to the acceleration in the water–ethanol system.

For the reaction between an ion and a neutral molecule, the rate constant is given by Eq. 12:[16]

$$\ln k = \ln k_0 + (Az^2/2RT\varepsilon_r)(r^{-1}-r_*^{-1}), \qquad (12)$$

where $A = N_A e^2/4\pi\varepsilon_0$. In Eq. 12, ε_r is a relative permittivity; r and r_*, the respective radii of the ion and the activated complex; z, a charge of the ion, and the others, the usual constants. Since $r_* > r$, the rate constant increases with a decrease in the permittivity of the solution. When r and r_* are independent of the temperature of reaction, the activation energy is given by:

$$E_a = E_0 - (Az^2/2)(r^{-1}-r_*^{-1})(1-bT)/\varepsilon_r, \qquad (13)$$

where b is given by $\varepsilon_r = c\exp(-bT)$ and where $E_0 = -R\mathrm{d}(\ln k_0)/\mathrm{d}(1/T)$. When b is calculated by means of the data of Albright and Gosting[17] and Akerlöf,[18] $(1-bT)/\varepsilon_r$ is negative and decreases with an increase in the alcohol contents. Thus, Eq. 13 indicates that E_a increases with an increase in the alcohol content. This prediction does not agree with the present results.

The changes in the solvation properties also have an important influence on the rate. Laidler and Eyring[19] and Scatchard[20] recognized the possible importance of specific solvation as a determining factor in the behavior of the rate constant. Hyne[21] ascribed the appearance of the maximum or the minimum in an activation energy to a specific solvation. According to him, the maximum appears as a result of the specific solvation

TABLE 4. THE VALUES OF THE RATE CONSTANT AND THE ACTIVATION PARAMETERS

Mole fraction of alcohol	k/M^{-1} s^{-1} 40 °C	30 °C	20 °C	10 °C	ΔH^* kJ mol^{-1}	ΔS^* J K^{-1} mol^{-1}	$\Delta(\Delta H^*)$[a] kJ mol^{-1}	$\Delta(-T\Delta S^*)$[b] kJ mol^{-1}
MeOH								
0.00	0.19	0.068	0.024	0.008	75±1	−20±1	—	—
0.10	0.27	0.094	0.031	0.009	80±1	−1±1	+5	−6
0.15	0.39	0.14	0.045	0.014	80±1	+1±1	+5	−6
0.22	0.61	0.22	0.075	0.024	77±1	−3±1	+2	−5
0.28	0.89	0.33	0.11	0.037	76±1	−5±1	+1	−5
0.47	2.5	0.95	0.33	0.11	75±1	+1±1	0	−6
0.95	8.0	3.2	1.2	0.40	71±1	−1±0	−4	−6
EtOH								
0.05	0.31	0.11	0.040	0.013	75±1	−15±3	0	−2
0.10	0.76	0.28	0.10	0.034	74±0	−12±1	−1	−2
0.17	1.8	0.72	0.26	0.086	73±1	−8±2	−2	−4
0.30	5.2	2.0	0.73	0.26	72±1	−4±3	−3	−5
0.52	9.4	3.8	1.6	0.64	63±1	−25±4	−12	+2
0.92	18	7.8	3.4	1.4	60±1	−32±3	−15	+4

a) $\Delta(\Delta H^*) = \Delta H^* - \Delta H^*(\text{in } H_2O)$. b) $\Delta(-T\Delta S^*) = -T\Delta S^* + T\Delta S^*(\text{in } H_2O)$.

when the reactant is an ionic species and when the transition state is a "dipole," which means also a charge-delocalized species. In the transition state, **1**, the negative charge must undergo delocalization preliminary to the electron transfer. A consideration of the transition state, **1**, as a "dipole" seems, therefore, a valid approximation. Then, the appearance of a maximum in ΔH^* can be expected. The small maximum in ΔH^* is possibly to be ascribed to the specific solvation in the water-methanol system. Though the relative permittivity suggests a larger maximum in the water–ethanol system than that in the water–methanol system,[21] the experimental results indicate that the maximum disappears in the former system.

Water forms a strong hydrogen bond to the O-atom in $HCOO^-$ and interferes with the approach of the iodine molecule to the ion. Since alcohol has a weak hydrogen-bonding property, the rate may be faster in alcohol than in water. Though DMSO has a greater permittivity than alcohols, it does not form a hydrogen bond, so the rate constant in DMSO is the largest among them.[1]

Hiller and Krueger observed that the ion-pairing of formate lowers the rate.[1] Since the ion-pair association constant increases with a decrease in the permittivity of a solvent, the ion-pairing effect lowers the rate with an increase in the alcohol content. This is not consistent with the present results.

Thus, the specific interactions of the solvent molecule with the reactants and the activated complex, such as the specific solvation or the hydrogen bond, possibly play an important role in the rate-determining step of Reaction 1.

References

1) F. W. Hiller and J. H. Krueger, *Inorg. Chem.*, **6**, 528 (1967).

2) R. A. Marcus, *J. Chem. Phys.*, **24**, 966 (1956).

3) F. Franks and J. G. Ives, *Quart. Rev. Chem. Soc.*, **20**, 1 (1966).

4) K. Hayakawa and S. Nakamura, *Bull. Chem. Soc. Jpn.*, **50**, 566 (1977).

5) R. O. Griffith and A. Mckeown, *Trans. Faraday Soc.*, **28**, 752 (1932).

6) E. Abel and K. Hilferding, *Z. Phys. Chem.*, **A172**, 353 (1935).

7) Hypohalous acid has been proposed for the oxidation of oxalate by bromine or chlorine; R. O. Griffith, A. Mckeown, and A. G. Winn, *Trans. Faraday Soc.*, **28**, 107 (1932); R. O. Griffith and A. Mckeown, *ibid.*, **28**, 518, 616 (1932).

8) J. N. Brønsted, *Z. Phys. Chem.*, **102**, 169 (1922).

9) N. Bjerrum, *Z. Phys. Chem.*, **108**, 82 (1924).

10) J. A. Christiansen, *Z. Phys. Chem.*, **113**, 35 (1924).

11) G. Scatchard, *Chem. Rev.*, **10**, 229 (1932).

12) C. W. Davies, "Progress in Reaction Kinetics," ed by G. Porter, Pergamon Press, New York (1961), p. 161.

13) J. D. Morrison, *J. Chem. Phys.*, **19**, 1305 (1951).

14) S. Nagakura and J. Tanaka, *Bull. Chem. Soc. Jpn.*, **32**, 734 (1959). The theory by which this conclusion is derived was proposed for the aromatic substitution reaction.

15) K. Fukui, T. Yonezawa, and H. Shingu, *J. Chem. Phys.*, **20**, 722 (1952); K. Fukui, T. Yonezawa, C. Nagata, and H. Shingu, *J. Chem. Phys.*, **22**, 1433 (1954).

16) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, New York (1961), p. 149.

17) P. S. Albright and L. J. Gosting, *J. Am. Chem. Soc.*, **68**, 1061 (1946).

18) G. Akerlöf, *J. Am. Chem. Soc.*, **54**, 4125 (1932).

19) K. J. Laidler and H. Eyring, *Ann. N. Y. Acad. Sci.*, **39**, 303 (1940).

20) G. Scatchard, *Ann. N. Y. Acad. Sci.*, **39**, 341 (1940).

21) J. B. Hyne, *J. Am. Chem. Soc.*, **82**, 5129 (1960).