Kinetics of Oxidation of Formic Acid by Silver(II) in Aqueous Perchloric Acid Solution

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The kinetics of oxidation of formic acid by silver(II) in acidic perchlorat emedia ($1.00 \leqslant [HClO_4] \leqslant 4.00$M) at 14.0, 22.0, and 30.0 °C have been investigated by means of a stopped-flow spectrophotometric technique. The experimental rate law, at constant [H⁺] and with formic acid in excess, is $-d[Ag^{II}]/dt = k_I{}^0[Ag^{II}][HCO_2H] + k_{II}{}^0[Ag^{II}]^2 + [HCO_2H][Ag^I]^{-1}$. The $[H^+]$ dependence of the terms is explained by taking into account the presence of the hydrolyzed species $[Ag(OH)]^+$ and $[Ag(OH)]^{2+}$: the corresponding hydrolysis equilibrium constants have been evaluated. The mechanism of the reaction is discussed in terms of different paths and reacting species. Comparison is made with previous findings concerning formic acid oxidation with other metal ions and oxidations with Ag^{II}.

SEVERAL papers deal with the kinetics and mechanisms of oxidations of formic acid with different metal ions,[1-3] and recent work has involved metal-ion couples of high redox potential such as Ce^{IV}–Ce^{III} (ref. 4) and Np^{VII}–Np^{VI} (ref. 5) in perchlorate media. The main features are the presence in the rate laws of terms dependent on and independent of acidity and the increase in reaction rate on increasing the redox potential of the oxidizing agent. In order to extend the available data, the oxidation with Ag^{II} in perchlorate media has been investigated.

The couple Ag^{II}–Ag^I is strongly oxidizing in aqueous-perchlorate media ($E^\ominus$ *ca.* 2.0 V).[6] Kinetic investigations of reactions of Ag^{II} with metal ions,[7] dithionate,[8] and hydroxylamines [9] have been reported and in these cases the kinetic laws contain terms involving $[Ag^{II}]$. On the other hand, the oxidation of water in different acidic media (perchlorate,[10] nitrate,[11] phosphate,[12] and sulphate [13]) and of phosphorous acid [14] showed a term dependent on $[Ag^{II}]^2$: this suggested a mechanism involving Ag^{III} formed *via* rapid disproportionation of Ag^{II}. The same disproportionation equilibrium is involved in Ag^{II}–Ag^I exchange.[15] However, the mechanism of oxidation of Tl^I with Ag^{II} in nitrate media, which involves the same $[Ag^{II}]^2$ dependence, has been explained in terms of intermediate formation of the NO_3 radical.[16]

EXPERIMENTAL

Reagents.—Formic acid solutions were prepared before use. Solutions of Ag^{II} were obtained by anodic oxidation of $Ag[ClO_4]$ [obtained by dissolving Ag_2O (Merck) in perchloric acid] in perchloric acid.[8,14] The total Ag^{II} concentration was determined spectrophotometrically at 470 nm ($\varepsilon_{Ag^{II}}$ 138 ± 2 l mol⁻¹ cm⁻¹ [17]). Sodium perchlorate (C. Erba) was used for adjustment of ionic strength. Twice distilled water was employed throughout.

Stoicheiometry.—It is generally accepted [1-5] that formic acid is oxidized by metal ions to carbon dioxide. In the present case the stoicheiometric equation can be represented as (1). This equation was tested in the stopped-flow

$$2\,Ag^{II} + HCO_2H \longrightarrow 2\,Ag^I + CO_2 + 2H^+ \qquad (1)$$

apparatus by mixing an Ag^{II} solution (whose concentration in excess, in the range 1×10^{-4}—3×10^{-3}M, was estimated spectrophotometrically) † with different amounts of HCO_2H and measuring the final absorbance at 470 nm which decreased toward zero on approaching the limiting ratio $[HCO_2H] : [Ag^{II}] = 2 : 1$.

Kinetics.—The kinetic determinations were made with a Durrum–Gibson stopped-flow spectrophotometer by following the disappearance of Ag^{II} at 470 nm. At this wavelength no other components of the investigated solutions contribute significantly to the measured absorbance. Formic acid was present in excess and the initial Ag^{II} concentration was determined spectrophotometrically before mixing the two reagents; the absorbance at the start of the reaction agreed with that of the calculated Ag^{II} concentration taking into account the dilution. An excess of Ag^I was always present in the Ag^{II} solution. The reaction traces were photographed on the storage screen of a Tektronix 564 oscilloscope. The kinetic data were evaluated with a weighted least-squares method.[18] The experiments were carried out at 14.0, 22.0, and 30.0 °C and $I = 4.0$M. The pathlength of the cell was 2.00 cm.

RESULTS

First-order Path.—By working with $[Ag^{II}]_0$ in the range 5×10^{-5}—20×10^{-5}M and in the presence of a large excess

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† 1 M = 1 mol dm⁻³, 1 cal = 4.184 J.

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of $[Ag]_T$ ($\geqslant 5 \times 10^{-2}$M), the disappearance of Ag^{II} obeyed first-order kinetics, *i.e.* plots of ln A_t against time (where A_t is the absorbance at time t) showed good linearity for at least three half-lives. This behaviour was independent of the initial Ag^{II} concentration. Pseudo-first-order rate constants, k_I (Table 1), were obtained from the gradients of the above plots by means of a weighted least-squares method; the standard deviation for each k_I value (obtained from triplicate runs) was generally within 2—4%.

TABLE 1

Values of the pseudo-first-order rate constant, k_I, at I = 4.0M, $[Ag^{II}]_0 = 5 \times 10^{-5}$—$20 \times 10^{-5}$M, and $[Ag]_T$ = 0.10M at 14.0 °C and 0.050M at 22.0 and 30.0 °C

θ_c/°C	$[HClO_4]$/ mol l^{-1}	$10^2[HCO_2H]$/ mol l^{-1}	k_I/s^{-1}
14.0	1.00	2.0	0.39
		4.0	0.92
		7.0	1.52
		10	2.07
	1.20	2.0	0.35
		4.0	0.74
		7.0	1.20
		10	1.70
	1.50	2.6	0.40
		6.5	1.03
		13	1.96
		26	3.63
		65	8.05
	2.00	2.6	0.30
		6.5	0.76
		13	1.47
		26	2.83
		65	6.62
	2.50	0.2	0.021
		0.4	0.039
		0.6	0.060
		5.0	0.46
		10	0.93
		20	1.68
		30	2.42
		50	4.26
	3.00	2.6	0.21
		6.5	0.49
		13	1.04
		26	2.03
		65	4.26
	4.00	2.6	0.16
		6.5	0.37
		13	0.76
		26	1.63
		65	3.68
22.0	1.00	2.0	1.06
		4.0	1.96
		7.0	3.42
		10	4.78
	2.00	2.0	0.69
		4.0	1.17
		7.0	2.12
		10	2.85
	3.00	2.0	0.41
		4.0	0.81
		7.0	1.43
		10	2.09
	4.00	2.0	0.36
		4.0	0.64
		7.0	1.11
		10	1.50
30.0	1.00	2.0	2.29
		4.0	4.53
		7.0	7.10
		10	10.8
	2.00	2.0	1.38
		4.0	2.64
		7.0	4.83
		10	6.90
	3.00	2.0	0.97
		4.0	1.89
		7.0	3.22
		10	4.83
	4.00	2.0	0.67
		4.0	1.40
		7.0	2.53
		10	3.68

Dependence on formic acid concentration. The pseudo-first-order rate constants (at constant $[H^+]$, $[Ag^I]$, and $[HClO_4]$) showed a linear dependence on $[HCO_2H]$ in the range 2.0×10^{-3}—0.650M. Thus, the observed rate law is as in (2). Second-order rate constants, k_I^0, calculated using

$$-d[Ag^{II}]/dt = k_I^0[Ag^{II}][HCO_2H] \qquad (2)$$

a weighted least-squares method, are in Table 2. The weights were based on the standard deviations of the pseudo-first-order rate constants.

TABLE 2

Values of second-order rate constant k_I^0(l mol^{-1} s^{-1}) at I = 4.0M

	$[HClO_4]$/mol l^{-1}						
θ_c/°C	1.00	1.20	1.50	2.00	2.50	3.00	4.00
14.0	21.5	17.5	14.5	11.2	9.2	8.0	6.1
22.0	48			30		21	15.5
30.0	108			68		48	35

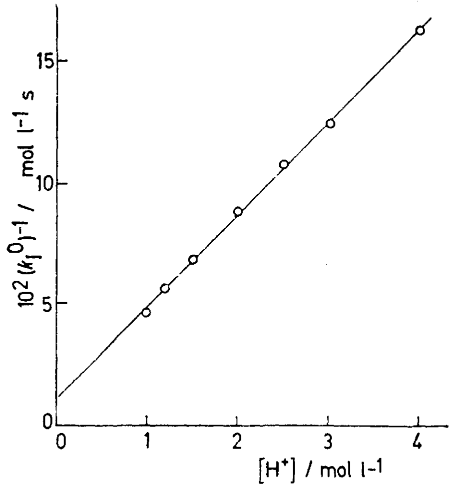

FIGURE 1 Plot of $1/k_I^0$ against $[H^+]$ at 14.0 °C and I = 4.0M

Hydrogen-ion dependence. At every temperature and constant $[Ag^I]$ and $[ClO_4]$ concentrations, plots of $1/k_I^0$ against $[H^+]$ gave straight lines (Figure 1). The overall rate law (3) can therefore be written where A and B are

$$-\frac{d[Ag^{II}]}{dt} = \frac{A[Ag^{II}][HCO_2H][H^+]^{-1}}{1 + B[H^+]^{-1}} \qquad (3)$$

constants. Values of A were 25 ± 3, 70 ± 6, and 165 ± 18 s^{-1} and for B 0.21 ± 0.05, 0.35 ± 0.11, and 0.48 ± 0.14 mol l^{-1} at 14.0, 22.0, and 30.0 °C respectively.

Dependence on silver(I) and perchlorate concentration. By working at constant $[H^+]$ and $[HCO_2H]$ the effect of varying $[Ag^I]$ was investigated at 14.0 °C (from 0.05 to 0.20M). No effect was found. The effect of perchlorate concentration was studied at 14.0, 22.0, and 30.0 °C and $[HClO_4]$ = 1.00M by varying the added quantity of $Na[ClO_4]$ from 0 to 3.0M. Again the rate of reaction was unaffected.

Second-order Path.—In kinetic runs with $[Ag^{II}]_0 > 2 \times 10^{-4}$M and small Ag^I concentrations and plotting ln A_t against time, deviations from a first-order dependence on $[Ag^{II}]$ were observed. Plots of reciprocal absorbance against time (for experiments at various $[HCO_2H]$ and $[HClO_4]$, and with $[Ag^{II}]_0 \geqslant 3 \times 10^{-4}$ and $[Ag]_T = 5 \times 10^{-3}$M) were linear in the early part of the reactions. Thus first and second-order paths in $[Ag^{II}]$ were assumed to be present, according to rate law (4). Integration of equation

$$-d[Ag^{II}]/dt = k_{II}[Ag^{II}]^2 + k_I[Ag^{II}] \qquad (4)$$

(4) gives (5)[19] which, by indicating the right-hand side as β,

$$\frac{k_I + k_{II}[Ag^{II}]}{k_I + k_{II}[Ag^{II}]_0} = \frac{[Ag^{II}]}{[Ag^{II}]_0} e^{k_I t} \qquad (5)$$

can be rewritten as (6). Straight lines were obtained on

$$1 - \beta = \frac{k_{II}}{k_I}([Ag^{II}]_0\beta - [Ag^{II}]_t) \qquad (6)$$

plotting $(1 - \beta)$ against $([Ag^{II}]_0\beta - [Ag^{II}]_t)$, and from the gradients k_{II} values were evaluated (Figure 2) (Table 3). At constant $[Ag^I]$, k_{II} was linearly dependent on $[HCO_2H]$ in the range 0.010—0.650M.

Dependence on silver(I) *concentration*. The rate of reaction decreased with increasing $[Ag^I]$. Since Ag^I is produced during the course of the reaction, an average value of $[Ag^I]$ for each experiment was estimated from the initial and final Ag^I concentrations. Data for experiments at constant temperature and $[H^+]$ are given in Figure 3 where k_{II} is plotted against $[HCO_2H]/[Ag^I]_{av}$. The linearity of the plots and the very small intercepts support the assumption that this path has a first-order dependence on $[HCO_2H]$ and an inverse dependence on $[Ag^I]$. The rate law of the second-

TABLE 3

Values of the rate constant k_{II} at $I = 4.0$M

θ_c/°C	$[HClO_4]$/mol l^{-1}	$10^3[Ag]_T$/mol l^{-1}	$10^3[Ag^{II}]_0$/mol l^{-1}	$[HCO_2H]$/mol l^{-1}	$10^{-3}k_{II}$/l mol^{-1} s^{-1}
14.0	1.00	5.0	0.56	0.020	2.3
		5.0	0.93	0.040	5.5
		5.0	0.75	0.070	8.4
	1.20	5.0	0.53	0.020	2.1
		5.0	0.73	0.040	4.8
		5.0	0.49	0.070	8.3
		5.0	0.46	0.10	11.6
		5.0	0.65	0.10	12.1
		6.5	0.94	0.10	8.8
		8.0	0.73	0.10	6.4
		10.0	0.76	0.10	6.1
		12.0	1.16	0.10	5.5
	1.50	5.0	1.38	0.10	10.2
		7.0	1.05	0.10	8.0
		10.0	1.14	0.10	5.2
		15.0	1.44	0.10	3.0
		20.0	0.94	0.10	2.5
	2.00	5.0	1.04	0.013	0.91
		5.0	1.64	0.039	2.6
		5.0	1.07	0.078	5.8
		5.0	1.78	0.13	10.8
		5.0	1.48	0.26	21
		5.0	1.32	0.65	49
		10.0	1.19	0.13	5.6
		30.0	1.38	0.13	1.7
	2.50	5.0	1.02	0.10	5.5
		5.0	0.39	0.10	6.6
		5.0	0.30	0.20	12
		5.0	0.28	0.30	16
		5.0	0.27	0.50	30
		6.5	1.29	0.10	5.1
		8.0	0.84	0.10	3.7
		10.0	1.27	0.10	3.5
		12.0	1.27	0.10	2.4
	3.00	5.0	1.25	0.013	0.72
		5.0	1.06	0.039	2.1
		5.0	1.03	0.078	3.3
		5.0	1.02	0.13	7.4
		5.0	0.93	0.26	13.5
		5.0	0.85	0.65	31
		5.0	1.21	0.10	4.4
		7.0	1.26	0.10	3.6
		10.0	1.00	0.10	2.5
		15.0	1.62	0.10	1.7
		20.0	0.94	0.10	1.3
		30.0	0.83	0.02	0.24
		30.0	1.28	0.04	0.39
		30.0	1.43	0.07	0.53
		30.0	1.24	0.10	0.69
		30.0	1.16	0.15	1.5
	3.50	5.0	1.19	0.10	5.0
		6.5	1.06	0.10	3.6
		8.0	0.73	0.10	2.7
		10.0	1.28	0.10	2.4
		12.0	1.35	0.10	1.8
	4.00	5.0	0.79	0.013	0.50
		5.0	1.19	0.039	1.4
		5.0	1.07	0.078	2.7
		5.0	1.28	0.13	4.6
		5.0	1.11	0.26	9.4
		5.0	0.99	0.65	21
		10.0	1.08	0.13	2.9
		30.0	1.48	0.13	1.1
22.0	1.00	5.0	1.19	0.05	14
		6.5	1.19	0.05	10.5
		8.5	1.44	0.05	8.0
		10.0	1.40	0.05	7.1
		15.0	1.89	0.05	4.4
	2.00	5.0	1.17	0.05	9.3
		6.5	1.61	0.05	6.8
		8.5	1.44	0.05	4.8
		10.0	1.89	0.05	3.8
		15.0	1.33	0.05	2.6
	3.00	5.0	1.54	0.05	5.8
		6.5	1.48	0.05	4.6
		8.5	1.65	0.05	3.5
		10.0	1.72	0.05	2.85
		15.0	1.33	0.05	1.85
	4.00	5.0	1.89	0.05	4.9
		6.5	1.29	0.05	3.45
		8.5	1.89	0.05	2.45
		10.0	1.57	0.05	1.9
		15.0	1.77	0.05	1.4
30.0	1.00	5.0	2.00	0.05	28
		6.5	1.97	0.05	21
		8.5	0.97	0.05	14.5
		10.0	0.94	0.05	13
		15.0	1.44	0.05	8.7
	2.00	5.0	1.01	0.05	15
		6.5	1.36	0.05	11.5
		8.5	0.87	0.05	9.2
		10.0	1.89	0.05	7.3
		15.0	1.40	0.05	5.1
	3.00	5.0	0.97	0.05	11
		6.5	1.26	0.05	7.6
		8.5	1.06	0.05	6.6
		10.0	1.65	0.05	5.3
		15.0	1.65	0.05	3.2
	4.00	5.0	1.44	0.05	9.2
		6.5	1.09	0.05	6.8
		8.5	1.40	0.05	5.8
		10.0	1.36	0.05	4.0
		15.0	2.06	0.05	3.1

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[19] Z. G. Szabo in 'Comprehensive Chemical Kinetics,' vol. 2, eds. C. H. Bamford and C. F. H. Tipper, Elsevier, Amsterdam, 1969.

order path can be represented as in (7). Values of k_{II}^0 are

$$-\,d[Ag^{II}]/dt = k_{II}^0[Ag^{II}]^2[HCO_2H]/[Ag^I] \qquad (7)$$

in Table 4. When very large amounts of Ag^I ($\geqslant 5 \times 10^{-2}$M) were present, the $[Ag^{II}]^2$ term was strongly depressed so that only the first points deviated from a pseudo-first-order treatment; k_I values (determined by neglecting the first points of the reaction traces) were in agreement with the previously reported values.

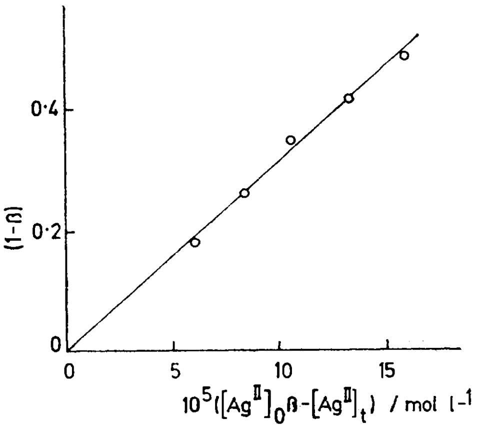

FIGURE 2 Plot, according to equation (6), at $[Ag^{II}]_0 = 1.40 \times 10^{-3}$, $[HCO_2H] = 0.050$, $[Ag]_T = 1.0 \times 10^{-2}$, $[HClO_4] = 1.00$, and $I = 4.0$M and 22.0 °C; the value adopted for k_I was 2.4 s^{-1}

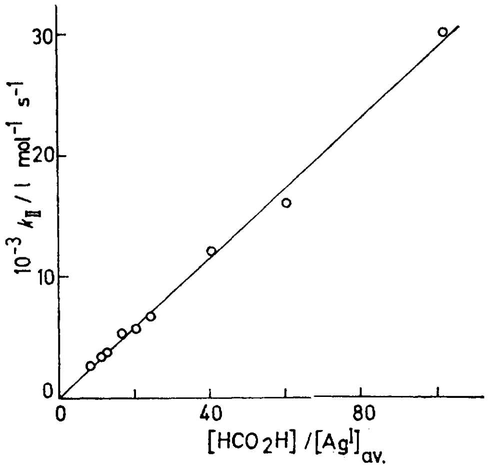

FIGURE 3 Plot of k_{II} as a function of $[HCO_2H]/[Ag^I]_{av}$ at $[Ag^{II}]_0 = 3 \times 10^{-4}$—$12 \times 10^{-4}$, $[Ag]_T = 5 \times 10^{-3}$—$12 \times 10^{-3}$, $[HCO_2H] = 0.10$—0.50, $[HClO_4] = 2.50$, and $I = 4.0$M and 14.0 °C

TABLE 4

Values of the second-order rate constant $10^{-2}\,k_{II}^0$ (l mol^{-1} s^{-1}) at $I = 4.0$M

	$[HClO_4]$/mol l^{-1}							
θ_c/°C	1.00	1.20	1.50	2.00	2.50	3.00	3.50	4.00
14.0	5.8	5.5	4.6	3.45	2.9	2.35	2.15	1.75
22.0	12.5			7.6		5.2		3.9
30.0	23			14		10		8.0

Hydrogen-ion dependence. Plots of $1/k_{II}^0$ against $[H^+]$ were linear with significant intercepts (Figure 4) and the overall rate law can be written as (8). Values obtained for C are $(7.8 \pm 1.4) \times 10^2$, $(1.7 \pm 0.3) \times 10^3$, and $(3.6 \pm 0.8) \times 10^3$ s^{-1} and for D 0.35 ± 0.12, 0.42 ± 0.18, and

$$-\frac{d[Ag^{II}]}{dt} = \frac{C[Ag^{II}]^2[HCO_2H][H^+]^{-1}}{(1 + D[H^+]^{-1})[Ag^I]} \qquad (8)$$

0.50 ± 0.22 mol l^{-1} at 14.0, 22.0, and 30.0 °C respectively. No effect of sodium perchlorate was observed ($I = 1.0$—4.0M).

Expression for the Kinetic Dependence on $[Ag^{II}]$.—In order to test the consistency of the previous findings, for various experimental conditions where both paths are present, the absorbance data were fitted to expression (9)

$$A_t = A_0\,\frac{k_I}{e^{k_It}(k_I + k_{II}[Ag^{II}]_0) - k_{II}[Ag^{II}]_0} \qquad (9)$$

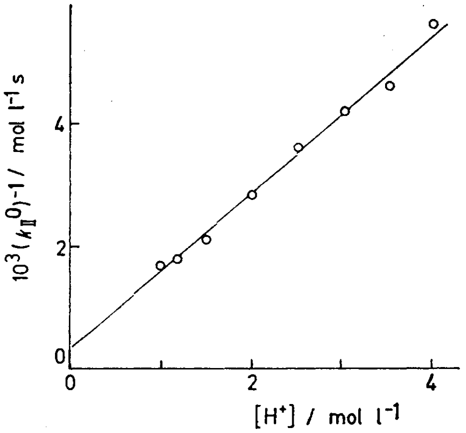

FIGURE 4 Plot of $1/k_{II}^0$ against $[H^+]$ at 14.0 °C and $I = 4.0$M

derived from (5); A_t is the absorbance at time t, A_0 and $[Ag^{II}]_0$ the initial absorbance and concentration of Ag^{II} respectively, and k_I and k_{II} are the rate constants of the first- and second-order paths. Figure 5 shows one fit obtained; the experimental absorbances were generally reproduced with an accuracy of ±5% over three half-lives.

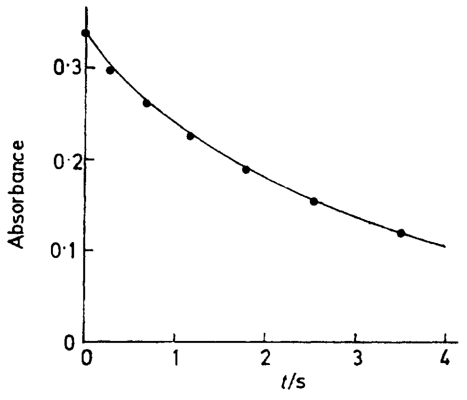

FIGURE 5 Typical fit of computed absorbances at various times with experimental (●) data; the computed line was evaluated according to equation (9) using $k_I^0 = 14.5$ and $k_{II}^0 = 4.6 \times 10^2$ l mol^{-1} s^{-1}. The solutions contained $[Ag^{II}]_0 = 1.23 \times 10^{-3}$, $[HCO_2H] = 0.013$, and $[Ag]_T = 5.0 \times 10^{-2}$M at 14.0 °C and $I = 4.0$M

Temperature Dependence.—Tables 2 and 4 collect the values of k_I^0 and k_{II}^0 at different temperatures. The overall activation enthalpies calculated by means of a weighted least-squares method are $\Delta H_I^{\ddagger} = 19 \pm 3$ and $\Delta H_{II}^{\ddagger} = 16 \pm 5$ kcal mol^{-1}.

DISCUSSION

Mechanism of the First-order Path.—The hydrogen-ion dependence can be explained taking into account the fact that Ag^{II} exists in the forms Ag^{2+} and $[Ag(OH)]^+$. Honig *et al.*[9] reported a large value for the hydrolysis constant of Ag^{2+} (0.32 ± 0.14 mol l^{-1} at 22 °C and $I = 5.95$M). Bearing in mind that at least four species are available for reaction, *i.e.* Ag^{2+}, $[Ag(OH)]^+$, HCO_2H, and HCO_2^-, the sequence (10)—(15) is proposed. If the

$$Ag^{2+}(aq) \overset{K_{10}}{\rightleftharpoons} [Ag(OH)]^+(aq) + H^+(aq) \qquad (10)$$

$$Ag^{2+} + HCO_2H \xrightarrow{k_{11}} Ag^I(aq) + \text{Radical} \qquad (11)$$

$$[Ag(OH)]^+(aq) + HCO_2H \xrightarrow{k_{12}} Ag^I(aq) + \text{Radical} \qquad (12)$$

$$Ag^{2+}(aq) + HCO_2^- \xrightarrow{k_{13}} Ag^I(aq) + \text{Radical} \qquad (13)$$

$$[Ag(OH)]^+(aq) + HCO_2^- \xrightarrow{k_{14}} Ag^I(aq) + \text{Radical} \qquad (14)$$

$$Ag^{II} + \text{Radical} \xrightarrow{k_{15}} Ag^I(aq) + CO_2 \qquad (15)$$

hydrolysis and dissociation equilibria and reaction (15) can be considered faster than reactions (11)—(14), rate law (16) can be derived where K_a is the dissociation

$$\frac{d[Ag^{II}]}{dt} = \frac{2(k_{11} + k_{12}K_{10}[H^+]^{-1} + k_{13}K_a[H^+]^{-1} + k_{14}K_{10}K_a[H^+]^{-2})[Ag^{II}]\,[HCO_2H]}{(1 + K_{10}[H^+]^{-1})(1 + K_a[H^+]^{-1})} \qquad (16)$$

equilibrium constant of formic acid. The expression reduces to (3) when $(k_{11} + k_{14}K_{10}K_a[H^+]^{-2}) \ll (k_{12}K_{10} + k_{13}K_a)[H^+]^{-1}$ and $K_a[H^+]^{-1} \ll 1$.[20] It follows that $A = 2(k_{12}K_{10} + k_{13}K_a)$ and $B = K_{10}$.

A sequence of the kind (10)—(15) has been previously suggested in the oxidation of formic acid with one-electron acceptor metal ions.[1-5] The variation in rate with [H+] for several cations suggests a major path involving loss of a proton. Although in several cases the formate ion has been proposed as reactant, this mechanism is not definitive. In other cases, such as Ce^{IV} (ref. 4) and Mn^{III},[3] a large contribution is due to a path involving precursor complexes between aquametal ions and undissociated acid. In the present case it is not possible to give a definitive assignment. The reaction proceeds more rapidly than those previously investigated, confirming a correlation between increasing rate and increasing redox potential of the metal-ion couple.

Mechanism of the Second-order Path.—This path can be explained if equilibrium (17) is taken into account.

$$2Ag^{II} \overset{K_{17}}{\rightleftharpoons} Ag^{III} + Ag^I \qquad (17)$$

This equilibrium lies far to the left.[10,21] The [H+] dependence can also be assigned to different reaction paths. In previously assessed mechanisms involving an $[Ag^{II}]^2$ dependence, strong dependences on [H+] have been found ($[H^+]^{-2}$),[10-13] attributed to highly solvated and hydrolyzed species of Ag^{3+}, such as $[AgO]^+$. If the Ag^{III} is present to a large extent as the hydrolyzed species $[Ag(OH)]^{2+}$ the sequence can (18)—(22) be proposed.

$$Ag^{3+}(aq) \overset{K_{18}}{\rightleftharpoons} [Ag(OH)]^{2+}(aq) + H^+(aq) \qquad (18)$$

$$Ag^{3+}(aq) + HCO_2H \xrightarrow{k_{19}} Ag^I(aq) + CO_2 \qquad (19)$$

$$[Ag(OH)]^{2+}(aq) + HCO_2H \xrightarrow{k_{20}} Ag^I(aq) + CO_2 \qquad (20)$$

$$Ag^{3+}(aq) + HCO_2^- \xrightarrow{k_{21}} Ag^I(aq) + CO_2 \qquad (21)$$

$$[Ag(OH)]^{2+}(aq) + HCO_2^- \xrightarrow{k_{22}} Ag^I(aq) + CO_2 \qquad (22)$$

Assuming the steps (17) [16,22] and (18) always equilibrated and in the light of the very small extent of Ag^{III} present,[10,21] rate law (23) can be deduced. As previously,

$$-\frac{d[Ag^{II}]}{dt} = \frac{2K_{17}(k_{19} + k_{20}K_{18}[H^+]^{-1} + k_{21}K_a[H^+]^{-1} + k_{22}K_{18}K_a[H^+]^{-2})[Ag^{II}]^2[HCO_2H]}{(1 + K_{18}[H^+]^{-1})(1 + K_a[H^+]^{-1})[Ag^I]} \qquad (23)$$

equation (23) agrees with rate law (8) if $k_{19} + k_{22}K_{18}K_a[H^+]^{-2} \ll (k_{20}K_{18} + k_{21}K_a)[H^+]^{-1}$ and $K_a[H^+]^{-1} \ll 1$; it follows that $C = 2K_{17}(k_{20}K_{18} + k_{21}K_a)$ and $D = K_{18}$.

The available data are not sufficient to distinguish between a reaction involving a two-equivalent step [reactions (19)—(22)] or two successive steps involving formation of Ag^{II} and a radical which is then further oxidized to the reaction products. With Tl^{III}(aq) and Hg_2^{2+}(aq) the oxidation of formic acid proceeds through intermediate-complex formation and *via* a single two-electron transfer step.[2] Such features could probably apply in the present case, although no experimental evidence was obtained. Similar kinetic behaviour, showing two competitive paths in $[Ag^{II}]$ and $[Ag^{II}]^2$, was found in the oxidation of water in nitrate media.[11a]

The present findings, using the previous assumptions, allow the hydrolysis equilibrium constants for Ag^{2+} and

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[20] L. G. Sillèn and A. E. Martell, 'Stability Constants of Metal–Ion Complexes,' *Special Publ.*, nos. 17 and 25, The Chemical Society, London, 1964 and 1970; C. F. Wells, *Trans. Faraday Soc.*, 1965, **61**, 2194; 1966, **62**, 2815; 1967, **63**, 147.

[21] J. A. McMillan, *Chem. Rev.*, 1962, **62**, 65.

[22] J. Pumies, W. Roebke, and A. Henglein, *Ber. Bunsengesellschaft Phys. Chem.*, 1968, **72**, 844.

Ag^{3+} to be estimated. In the oxidation of water [10-13] (which involves an $[H^+]^{-2}$ dependence), the active form of Ag^{3+} is $[AgO]^+$, but the oxidation of phosphorous acid showed a more complex inverse dependence on $[H^+]$.[14] The present data indicate that the first hydrolysis constant of Ag^{3+} is large, but give no information on the second hydrolysis constant.

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