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Kinetics and Mechanism of the Oxidation of Formic Acid by Silver(II) in Nitric Acid Media

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The kinetics and mechanism of the oxidation of formic acid by silver(II) in 0.71–6.3 M nitric acid has been investigated utilizing the stopped-flow technique. Over the entire range of conditions studied the observed rate law is of the form $-{}^1/{}_2d[Ag(II)]/dt = k[Ag(II)][HCO_2H]_T/(1 + K_5[NO_3^-]_0)[H^+]_0$. A mechanism is proposed in which the reaction occurs through two one-electron-transfer steps. The formyl free radical is formed in the first step and then reacts further to produce the reaction products.

Introduction

Silver(II) is an exceptionally powerful oxidant with a Ag(II)–Ag(I) potential of +1.93 V in 4 M nitric acid and +1.97 V in 4 M perchloric acid at 25 °C.[1] Numerous studies have been reported of silver(II) reactions with a variety of inorganic substrates, i.e., Fe(II), Co(II), Ce(III),[2] Mn(II),[2,3] V(IV),[2,4] Tl(I),[5] Cr(III),[3,6] NH_3,[7] NH_2OH,[8] H_3PO_3,[9] and $S_2O_6^{2-}$.[10] In addition to studies involving the reaction of silver(II) with the above species its reduction by water in the presence of HNO_3,[11] $HClO_4$,[12,13] H_2SO_4,[14] and H_3PO_4[15] has been examined.

Similarly the oxidation of formic acid has been investigated using various inorganic oxidants. Among those studied were Hg^{II}_2, Hg(II),[16] Tl(III),[16,17] Co(III),[18,19] Mn(III),[20,21] Ce(IV),[22,23] V(V),[19,24] Cr(VI),[19,25] Np(VII),[26] MnO_4^-,[16,27-29] and $S_2O_8^{2-}$. In many of these studies it has been observed that the oxidation of formic acid can occur either through two successive one-electron-transfer steps[16,18,19,21-25] or alternatively via a two-electron-transfer step.[17,22,27-29] In some of these reactions there was evidence that a complex ion intermediate was formed.[17,19,20,22-25]

The present work was initiated in order to elucidate the mechanism by which silver(II) oxidizes formic acid. For the reaction of silver(II) with formic acid a sequence of two one-electron-transfer steps could be visualized. Alternatively, if silver(III), produced from the rapid disproportionation of silver(II),[11] is a reactive species, then formic acid would most likely be oxidized in a single two-electron-transfer step.[12,15] In addition, for either of these cases, complex ion formation could conceivably be involved in the reaction pathway.

In view of the limited amount of kinetic studies involving the reaction of silver(II) with any organic substrate, reported to date, it would be of interest to investigate the kinetics and mechanism of the oxidation of this simple monocarboxylic acid by silver(II).

Experimental Section

Materials and Methods. All chemicals used were either reagent grade or of certified purity.

In all kinetic experiments silver(II) solutions were prepared immediately before use in nitric acid from silver(II) oxide[11] (Alfa Inorganics, Ventron Corp.). The concentration of the silver(II) solutions were determined rapidly and conveniently using a method previously reported.[5,12] The procedure involved the quantitative oxidation of cerium(III) to cerium(IV) by silver(II) followed by the photometric determination of the cerium(IV) concentration at fixed nitric acid concentration.

Formic acid (90.3%, Fisher Chemical Co.) solutions were made up just prior to use in standardized nitric acid solutions. In most solutions the ionic strength was maintained constant using the appropriate amounts of nitric acid and sodium nitrate. In those runs where the nitrate ion dependency was determined, nitric acid and perchloric acid were both used to maintain constant acidity while allowing the nitrate ion concentration to be varied at constant ionic strength. Several runs were made to determine the silver(I) dependency using silver(I) nitrate dissolved in nitric acid solution.

Table I. CO_2:Ag(II) Mole Ratio[a]

Amt × 10^3, mol		
Ag(II)	CO_2	CO_2:Ag(II)[b]
0.293	0.15	1:1.9
0.954	0.49	1:1.9
1.89	0.97	1:2.0

[a] All experiments were performed with $[HNO_3] = 6.18$ M, $[HCO_2H]_T = 0.239$ M, and $\mu = 6.3$ M, at 25 °C. [b] Reported values for each experiment are the average of at least three replicate determinations. The values were reproducible to within about 2%. The total volume of the reaction mixture for each run was 40 ml.

Stoichiometry. A dual-buret gas apparatus previously described[30] was used to measure carbon dioxide evolution. Several runs were carried out to confirm that in the absence of silver(II) no decomposition of formic acid in nitric acid occurred within the time of the experiment.

Kinetic Measurements. The Aminco-Morrow stopped-flow apparatus[31] was used for all kinetic runs in conjunction with an Aminco Minimonochromator. An 0.8-cm path length cell was used. The detector used was a Hamamatsu R-136 photomultiplier tube (PMT) powered by an Aminco photomultiplier high-voltage power supply. The PMT output signal was fed into an Aminco Linear-Log Photometer and the logarithmic signal (absorbance) was displayed using a Tektronix 5103N storage oscilloscope. For most kinetic runs the rate of silver(II) loss was monitored at 365 nm. For higher silver(II) concentrations where the absorbance at 365 nm (ϵ 2068 ± 39 M^{-1} cm^{-1}) is too great, the reaction was followed at 685 nm (ϵ 269 ± 4 M^{-1} cm^{-1}). The molar absorptivities were determined in 6.11 M nitric acid solution. In a number of cases the kinetics were followed at both wavelengths for identical reaction mixtures. Invariably the shape of the kinetic traces and the calculated rate constants were found to be identical indicating that the same process was being observed at both 365 and 685 nm. All kinetic determinations were made at 25.0 ± 0.1 °C with the ionic strength $\mu \simeq 6.3$ M.

Results

Stoichiometry. The results in Table I are consistent with the reaction $2Ag(II) + HCO_2H \rightarrow 2Ag(I) + CO_2 + 2H^+$. The stoichiometry was determined under conditions similar to those established for the kinetic experiments. In all determinations the mole ratio of carbon dioxide evolved to silver(II) consumed was found to be 1:2. Analogous stoichiometric results have been previously found for the oxidation of formic acid by most other inorganic oxidants.[16-18,20-22,25,28]

Kinetics. Under the experimental kinetic conditions with Ag(II) in limiting quantity, the reaction was found to be first order in silver(II) in the concentration range of 0.404×10^{-3} to 9.74×10^{-3} M, first order in formic acid (Table II), and zero order in silver(I) in the concentration range of 0.32×10^{-3} to 40.0×10^{-3} M.

The observed pseudo-first-order rate constant, k_{obsd}, is defined by eq I. The second-order rate constant, $k_{H,N}$, which

$$-d[Ag(II)]/dt = k_{obsd}[Ag(II)] \qquad (I)$$

Table II. Dependence of k_{obsd} on Formic Acid[a]

$10^3[Ag(II)]_0$, M	$10^2[HCO_2H]_T$, M	k_{obsd}, s^{-1}	$k_{H,N}$, M^{-1} s^{-1}
0.799	0.838	0.0261	3.11
0.823	1.20	0.0374	3.12
0.823	2.39	0.0677	2.83
0.820	4.79	0.149	3.11
2.00	4.79	0.159	3.32
0.807	5.98	0.177	2.96
0.826	9.57	0.300	3.13
2.00	9.57	0.304	3.17
0.840	12.0	0.338	2.82
0.807	23.9	0.700	2.93
0.807	35.9	1.07	2.98
0.823	47.9	1.41	2.94

[a] $[HNO_3]_0 = 6.00$ M and $\mu = 6.3$ for all experiments. Silver(I) was not added to the reaction mixture in these experiments.

Table III. Dependence of $k_{H,N}$ on the Hydrogen Ion Concentration[a]

$[HNO_3]_0$, M	k_{obsd}, s^{-1}	$k_{H,N}$, M^{-1} s^{-1}	$[HNO_3]_0$, M	k_{obsd}, s^{-1}	$k_{H,N}$, M^{-1} s^{-1}
0.711	3.37	28.1	3.97	0.643	5.36
1.17	2.03	16.9	4.27	0.469	3.91
1.42	1.57	13.1	4.98	0.450	3.75
1.98	1.24	10.3	5.69	0.389	3.24
2.84	0.967	8.06	6.17	0.371	3.09
3.55	0.779	6.49	6.38	0.353	2.94

[a] $\mu = 6.3$ M for all runs. The concentrations of formic acid and silver(II) were held constant at $[HCO_2H]_T = 0.120$ M and $[Ag(II)]_0 = 2.0 \times 10^{-3}$ M.

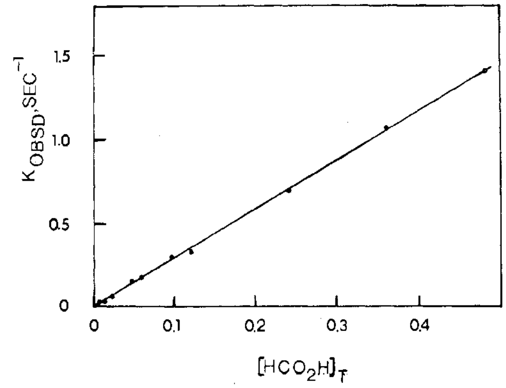

Figure 1. Plot of k_{obsd} vs. $[HCO_2H]_T$.

incorporates both the hydrogen ion and nitrate ion dependencies is given by eq II. The constancy of $k_{H,N}$ (Table II)

$$k_{obsd} = k_{H,N}[HCO_2H]_T \qquad (II)$$

with varying $[HCO_2H]_T$ confirms the first-order formic acid dependency. The plot of k_{OBSD} vs. $[HCO_2H]_T$ (Figure 1) is linear with a slope, $k_{H,N}$, equal to 2.95 ± 0.13 M^{-1} s^{-1} and an intercept of zero.

Acidity Dependency. At constant nitrate ion concentration the second-order rate constant $k_{H,N}$ was found to be inversely related to the hydrogen ion concentration (Table III). This inverse dependency is given by the relationship in eq III, where

$$k_{H,N} = A/[H^+]_0 \qquad (III)$$

A is the proportionality constant. The plot of $k_{H,N}$ vs. $1/[H^+]_0$ is shown in Figure 2. The slope, A, is 19.8 ± 1.5 s^{-1} and the intercept is zero in the acidity range 0.711–6.28 M.

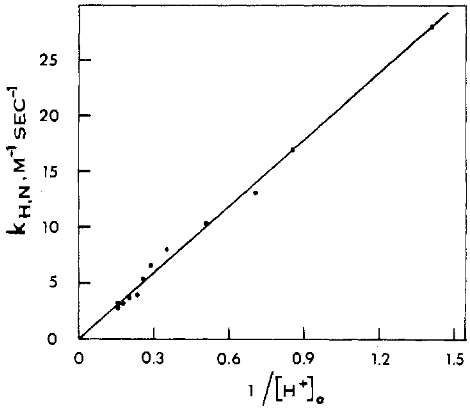

Figure 2. Plot of $k_{H,N}$ vs. $1/[H^+]_0$.

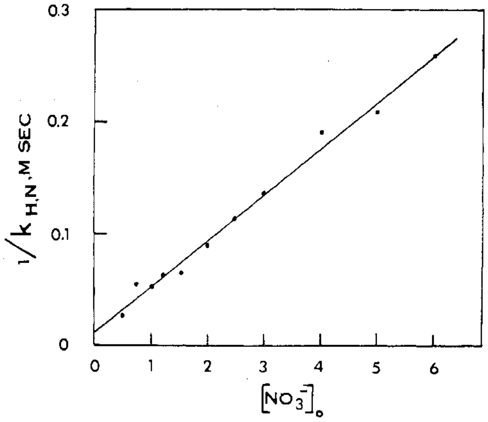

Figure 3. Plot of $1/k_{H,N}$ vs. $[NO_3^-]_0$.

Table IV. Dependence of $k_{H,N}$ on the Nitrate Ion Concentration[a]

$[ClO_4^-]_0$, M	$[NO_3^-]_0$, M	k_{obsd}, s^{-1}	$k_{H,N}$, M^{-1} s^{-1}
0.00	6.00	0.462	3.85
0.986	4.98	0.568	4.73
2.00	4.00	0.630	5.25
3.00	3.00	0.877	7.31
3.52	2.49	1.05	8.75
4.00	2.00	1.35	11.3
4.46	1.53	1.85	15.4
4.79	1.22	1.93	16.1
5.00	1.00	2.27	18.9
5.26	0.712	2.17	18.1
5.50	0.500	4.80	40.0

[a] $[H^+]_0 = 6.00$ M and $\mu = 6.0$ M for all experiments. The concentrations of formic acid and silver(II) were held constant at $[HCO_2H]_T = 0.120$ M and $[Ag(II)]_0 = 1.6 \times 10^{-3}$ M. The $[NO_3^-]_0$ and $[ClO_4^-]_0$ values were obtained from appropriate mixtures of nitric acid and perchloric acid solutions as discussed in the Experimental Section.

Nitrate Ion Dependency. Table IV shows the effect on $k_{H,N}$ of varying the nitrate ion concentration at constant acidity. The data were found to obey eq IV. B and K are constants

$$k_{H,N} = B/(1 + K[NO_3^-]_0) \qquad (IV)$$

independent of the nitrate ion concentration. The linear form of eq IV is

$$1/k_{H,N} = (K/B)[NO_3^-]_0 + 1/B \qquad (V)$$

A plot of $1/k_{H,N}$ vs. $[NO_3^-]_0$ is shown is Figure 3. The plot is linear with a slope, K/B, equal to 0.042 ± 0.001 s and an intercept, $1/B$, of 0.011 ± 0.008 M s. The calculated value of K is 3.8 ± 0.7 M^{-1}.

Mechanism and Discussion

A mechanism consistent with our results is

$$Ag^{2+} + HCO_2^- \rightarrow Ag^+ + HCO_2\cdot \quad k_1 \qquad (1)$$

$$Ag^{2+} + HCO_2\cdot \rightarrow Ag^+ + H^+ + CO_2 \quad \text{fast} \qquad (2)$$

where step 1 is the rate-determining step. Appropriate combination of the above steps along with the equilibria

$$HCOOH \rightleftharpoons H^+ + HCO_2^- \quad K_3 \qquad (3)$$

$$Ag^{2+} + NO_3^- \rightleftharpoons AgNO_3^+ \quad K_4 \qquad (4)$$

yields the rate law

$$-\frac{1}{2}\frac{d[Ag(II)]}{dt} = \frac{k_1K_3[Ag(II)][HCOOH]_T}{(1 + K_4[NO_3^-]_0)[H^+]_0} \qquad (VI)$$

The literature values for K_3 and K_4 are 1.77×10^{-4} M[32] and 0.94 M^{-1},[33] respectively.

The participation of Ag(III) has been ruled out by the fact that the $[Ag(I)]_0$ has no measurable effect on the observed rate constant.

The rate expression from eq VI predicts all of the dependencies previously noted and found. This means that k_{obsd} defined by eq I is

$$k_{obsd} = \frac{2k_1K_3[HCO_2H]_T}{(1 + K_4[NO_3^-]_0)[H^+]_0} \qquad (VII)$$

and

$$k_{H,N} = \frac{2k_1K_3}{(1 + K_4[NO_3^-]_0)[H^+]_0} = \frac{k_{obsd}}{[HCO_2H]_T} \qquad (VIII)$$

Also, at constant nitrate ion concentration the proportionality constant A from eq III is

$$A = \frac{2k_1K_3}{1 + K_4[NO_3^-]_0} \qquad (IX)$$

while at constant acidity

$$B = 2k_1K_3/[H^+]_0 \qquad (X)$$

and $K = K_4$. The calculated value of k_1 from eq VI is $3.9 \pm 0.3 \times 10^5$ M^{-1} s^{-1}.

The Ag^{2+} species is apparently much more reactive than the $AgNO_3^+$ species, and so as the $[NO_3^-]_0$ increases, the concentration of the more reactive Ag^{2+} species decreases and the observed rate of reaction decreases.

A free-radical scavenger, acrylamide, was used to detect the presence of the free radical formed in step 1 and consumed in step 2. In the presence of acrylamide the CO_2:Ag(II) mole ratio should decrease if the free-radical is present.[34] The results are shown in Figure 4 and confirm the presence of a free-radical species.

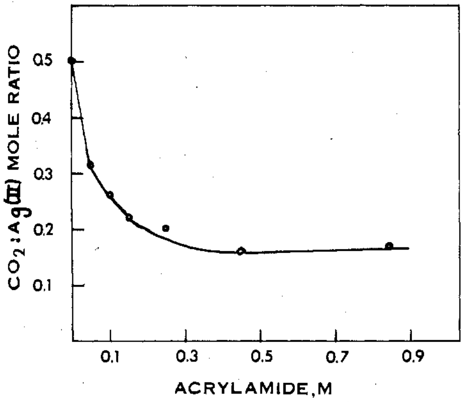

Figure 4. Effect of acrylamide on the CO_2:Ag(II) mole ratio; $[HCO_2H]_T = 0.239$ M, $[Ag(II)]_0 = 1.2 \times 10^{-2}$ M, and $[HNO_3]_0 = 6.32$ M.

It is worth noting that the mole ratio approaches a limiting value of 0.15 rather than zero. This type of behavior was also observed by others[34] but not explained. A possible explanation is that a second but minor reaction pathway exists in which a free radical is not formed. Thompson and Sullivan[26] in their study of the neptunium(VII)–formic acid reaction interpreted their results in terms of a two-electron rate-determining transfer step in which a free radical is not formed. This may also be possible for the silver(II) system in which the two-electron reduction of Ag^{2+} to yield Ag^0 is the rate-determining step followed by the oxidation of Ag^0 by Ag^{2+}. This is made plausible since the Ag^{2+}–Ag^0 reduction potential is ~1.4 V. It is possible to conceive of an alternate mechanism in which the elementary steps 5 and 6 occur. As in the first possibility

$$Ag^{2+} + HCO_2^- \rightleftharpoons AgHCO_2^+ \quad K_5 \qquad (5)$$

$$AgHCO_2^+ + Ag^{2+} \rightarrow 2Ag^+ + CO_2 + H^+ \quad k_6 \qquad (6)$$

a free radical is not formed. Both of the above pathways, properly treated, result in a rate expression of the correct form.

In summary, a reaction pathway involving two successive one-electron-transfer steps has been presented. Other possible pathways such as

$$Ag^{2+} + HCO_2^- \rightleftharpoons AgHCO_2^+ \quad K_7 \qquad (7)$$

$$AgHCO_2^+ \rightarrow Ag^+ + HCO_2\cdot \quad k_8 \qquad (8)$$

$$Ag^{2+} + HCO_2\cdot \rightarrow Ag^+ + CO_2 + H^+ \quad \text{fast} \qquad (9)$$

have not been discussed since there is no evidence to support the presence of a $AgHCO_2^+$ complex ion intermediate, although other metal ions such as Mn(III),[20] Ce(IV),[23,24] and Cr(VI)[25] have been shown to form metal ion–formate ion complexes.

Registry No. Ag(II), 15046-91-0; HCO_2H, 64-18-6; NO_3^-, 14797-55-8.

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