Kinetics and Mechanism of the Oxidation of Formic Acid by Methyltributylammonium Permanganate in Methylene Chloride Solutions

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The oxidation of formic acid by methyltributylammonium permanganate in methylene chloride solutions is strongly autocatalyzed by one of the reaction products, colloidal manganese dioxide. The rate law for the catalytic reaction is first-order with respect to the catalyst and follows the Langmuir isotherm for the adsorption of both the oxidizing and the reducing agents on its surface. The noncatalytic reaction is also first order with respect to permanganate. Both mechanisms are dramatically inhibited by the presence of water, and both also exhibit a primary kinetic isotope effect for the oxidation of DCOOH. Possible mechanisms, consistent with the experimental information, are discussed.

Introduction

The oxidation of formic acid and formate ion by permanganate ion in aqueous media has been studied in some detail with respect to the reaction mechanisms.[1-8] In order to augment the information available, we have undertaken a kinetic study of the permanganate oxidation of formic acid in a nonpolar organic solvent, methylene chloride, using methyltributylammonium permanganate as the oxidizing agent.[9] Under these conditions, it was discovered that the reaction is an autocatalytic process.

Several permanganate oxidations in aqueous media have also been reported to take place autocatalytically; for example, the oxidation of manganous ion,[10] hydrogen peroxide,[11] oxalic acid,[12,13] aliphatic amines,[14,15] amino acids,[16] aromatic aldehydes,[17] and ketones[18] as well as the decomposition of permanganate ion under neutral and acidic conditions[19] have been reported to exhibit some evidence of autocatalysis. Little information regarding the corresponding reactions in nonaqueous solvents is available, other than the recent report that the oxidation of 1-tetradecene in methylene chloride is also slightly autocatalytic.[20] However, because a greater fraction of the total reaction proceeds by way of the catalytic mechanism, the oxidation of formic acid offers a better opportunity to study the autocatalytic phenomenon.

Experimental Section

The solvent, methylene chloride, was purified by double distillation over 4A molecular sieves. The oxidizing agent, methyltributylammonium permanganate was obtained by precipitation from an aqueous mixture of methyltributylammonium bromide and potassium permanganate.[21] Formic acid and the other organic substrates are commercially available compounds. The kinetic runs were all performed under pseudo-first-order conditions, in the presence of an excess of reducing agent.

The disappearance of permanganate was followed by monitoring its absorbance at 526 nm (ϵ 2.63 × 10^3) with a Hewlett-Packard 8450A UV-VIS spectrophotometer, and the kinetic data were analyzed by using the initial reaction rate approach. The absorbance due to the reaction product was estimated in order to calculate correct permanganate concentrations,[22] and corrections were made for the contribution to the initial rate from the slow reduction of permanganate by the solvent.[20]

In a typical experiment, a solution of formic acid (3.18×10^{-2} M) in methylene chloride, contained in a 50-mL flask, was held in a thermostated bath for about 10 min. Then, methyltributylammonium permanganate (5×10^{-3} g) was added, and the solution was homogenized by stirring vigorously. About 2 mL of the solution was immediately transferred to a cell (at 25.0 °C) in the thermostated compartment of the spectrophotometer. The solution was periodically scanned, and the absorbances were recorded while the reaction progressed.

The oxidation state of manganese at the end of the reaction was determined by means of an iodometric technique. When the spectrophotometer showed that all of the permanganate had been reduced, a 5-mL aliquot was transferred to another flask, and an excess of tetrabutylammonium iodide (2×10^{-2} g) was added along with acetic acid (5 mL). The yellow mixture thus obtained was diluted to 50 mL with methylene chloride, and the quaternary ammonium triiodide concentration was determined by measuring its absorbance at 365 nm (ϵ 2.62 × 10^4).

Results

Sequential scans of the reaction solution, shown in Figure 1, exhibit an isosbestic point at 468 nm with only a very slight shift to lower wavelengths near the end of the reaction.

Iodometric determinations indicated that the apparent oxidation state of manganese in the product mixtures is

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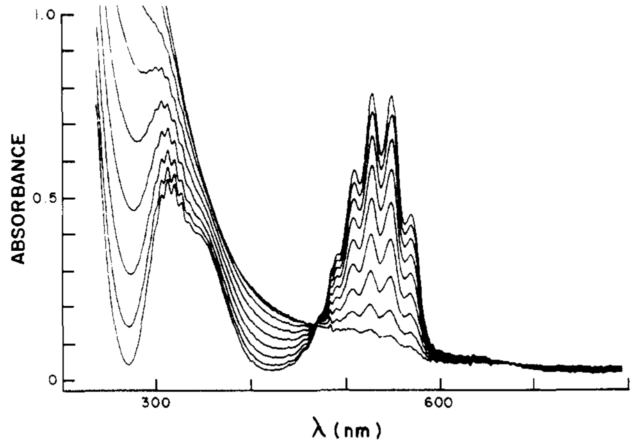

Figure 1. Successive scans, at 3-min intervals, for the oxidation of formic acid (2.12 × 10^{-2} M) by methyltributylammonium permanganate (2.98 × 10^{-4} M) in methylene chloride at 25.0 °C (isosbestic point = 468 nm).

Table I. Kinetic Data for the Catalytic Oxidation of Formic Acid at Several Concentrations of Manganese Dioxide[a]

$[MnO_2]_i$,[b] M × 10^4	$-d[QMnO_4]_i/dt$,[c] M s^{-1} × 10^6	k_1,[d] s^{-1} × 10^3
1.37	0.95	6.93
2.19	1.61	7.35
2.95	2.04	6.92
3.60	2.58	7.17
4.26	2.97	6.97

[a] $[QMnO_4]_i$ = 3.00 × 10^{-4} M; [HCOOH] = 2.12 × 10^{-2} M; temperature = 25.0 °C; solvent = CH_2Cl_2. [b] Initial concentration of manganese products [Mn(II) + Mn(IV)] obtained from the reduction of $QMnO_4$ in a preceding experiment. [c] Initial rate for the catalytic reaction. [d] Pseudo-first-order rate constants for the catalytic reaction defined as, $k_1 = (-d[QMnO_4]/dt)_i/[MnO_2]_i$.

+3.25 ± 0.06. The spectrum recorded at the end of the reaction is that of a colloid, as shown by the fact that the absorbance decreases with the fourth power of the wavelength (Figure 2), in good accordance with Rayleigh's law[23] for scattering (as opposed to absorption) of light. Thus, the products obtained from the reduction of permanganate are most probably a mixture of colloidal MnO_2 and soluble manganese(II), the former being responsible for the light-scattering phenomenon.

A plot of the reaction rate vs time exhibited a bell-shaped profile, characteristic of autocatalytic reactions.[24] A typical example is shown in Figure 3a. If fresh permanganate is added to the solution at the end of the reaction, a dramatic increase in the initial rate is observed and the reaction rate vs time plot loses the bell-shaped feature (see Figure 3b). This behavior is also characteristic of autocatalytic reactions.

The initial rate for the uncatalyzed reaction was obtained by taking a tangent to a plot of absorbance vs time at time zero. The rates for the catalyzed reaction were then obtained by repeating the experiment in the presence of various concentrations of MnO_2 and subtracting the known rate for the uncatalyzed reaction. Manganese dioxide was obtained either from previously completed experiments or from the photolysis of methyltributylammonium permanganate in methylene chloride.[25] The rate of the catalyzed reaction, as the data in Tables I and II indicate, is directly proportional to the amount of MnO_2 present in the solution.

Table II. Initial Rates in the Absence and Presence of Catalyst[a]

[catalyst],[b] M × 10^4	$-d[QMnO_4]/dt_i$, M s^{-1} × 10^7
0.00	0.35
3.00	2.24

[a] $[QMnO_4]_i$ = 3.00 × 10^{-4} M; [HCOOH] = 5.30 × 10^{-3} M; temperature = 25.0 °C; solvent = CH_2Cl_2. [b] The catalyst (a soluble form of colloidal MnO_2) was obtained by photochemical reduction of $QMnO_4$ in CH_2Cl_2.

Table III. Kinetic Data for the Noncatalytic Oxidation of Formic Acid[a]

$[QMnO_4]_i$,[b] M × 10^4	$-d[QMnO_4]/dt$,[c] M s^{-1} × 10^6	k_1,[d] s^{-1} × 10^3
0.71	0.26	3.66
1.37	0.49	3.58
2.19	0.85	3.88
2.95	1.12	3.80
3.60	1.37	3.81

[a] [HCOOH] = 2.12 × 10^{-2} M; temperature = 25 °C; solvent = CH_2Cl_2. [b] Initial permanganate concentration. [c] Initial rate for the noncatalytic reaction. [d] Pseudo-first-order rate constants for the noncatalytic reaction defined as $(-d[QMnO_4]/dt)_i/[QMnO_4]_i$.

Table IV. Kinetic Data for the Noncatalytic Oxidation at Several Formic Acid Concentrations[a]

[HCOOH], M × 10^2	$-d[QMnO_4]/dt$,[b] M s^{-1} × 10^7	k(×10^2),[c] M^{-1} s^{-1}
0.53	0.35	2.20
1.06	0.66	2.08
2.12	1.08	1.70
3.18	1.48	1.55
4.24	1.75	1.38
5.30	2.10	1.32
6.36	2.45	1.28

[a] $[QMnO_4]_i$ = 3.00 × 10^{-4} M; temperature = 25.0 °C; solvent = CH_2Cl_2. [b] Initial rate for the noncatalytic reaction. [c] rate constant for the noncatalytic reaction, defined as $k = (-d[QMnO_4]/dt)_i/[QMnO_4]_i[HCOOH]$.

Table V. Kinetic Data at Several Water Concentrations[a]

$[H_2O]$, M × 10^2	$rate_i$, M s^{-1} × 10^7	$rate_i$, M s^{-1} × 10^7
0.00	2.10	27.36
0.23	1.51	17.96
0.46	1.34	14.26
1.14	1.14	7.63
2.28	1.01	3.90
3.41	0.90	2.83
4.56	0.83	2.31
5.70	0.76	1.75

[a] $[QMnO_4]_i$ = 3.00 × 10^{-4} M; [HCOOH] = 5.30 × 10^{-2} M; temperature = 25.0 °C; solvent = CH_2Cl_2. [b] Initial rate for the noncatalytic reaction. [c] Initial rate for the catalyzed reaction in the presence of manganese dioxide (3.00 × 10^{-4} M) at the beginning of the reaction.

Table VI. Deuterium Isotope Effects[a]

reaction	HCOOH/DCOOH[b]	HCOOH/HCOOD[b]
noncatalytic	4.1 ± 0.2	1.34 ± 0.02
catalytic[c]	10.7 ± 0.6	1.33 ± 0.05

[a] $[QMnO_4]_i$ = 3.00 × 10^{-4} M; [HCOOH] = [DCOOH] = [HCOOD] = 2.12 × 10^{-2} M; temperature = 25.0 °C; solvent = CH_2Cl_2. [b] quotient between the corresponding initial rates. [c] In the presence of manganese products (3.00 × 10^{-4} M) at the beginning of the reaction.

As illustrated in Figures 4 and 5, there is a reciprocal relationship between the rates of the catalyzed reaction

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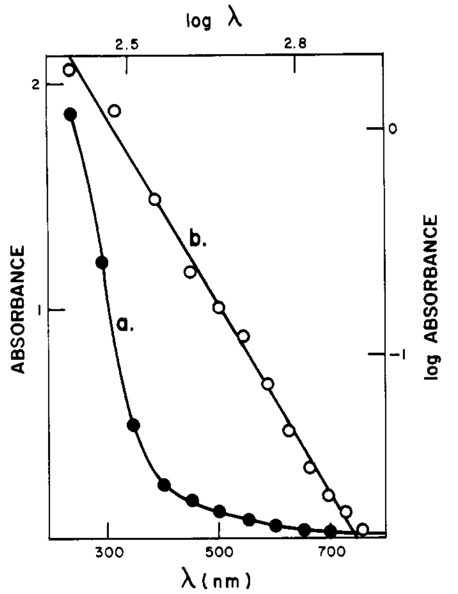


Figure 2. Spectrum (a) and log A vs log λ relationship (b) for the product obtained from the reduction of methyltributylammonium permanganate (3.08×10^{-4} M) by formic acid (6.36×10^{-2} M) in methylene chloride at 25.0 °C (slope −4.23, $r = 0.997$).

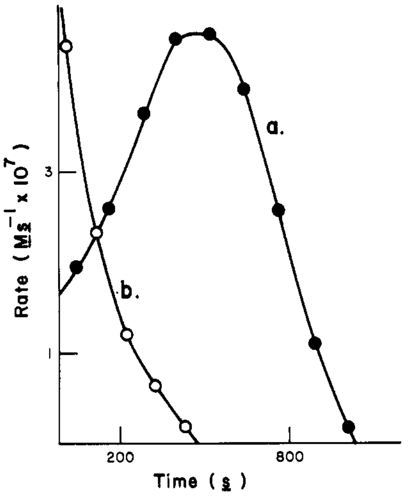


Figure 3. Reaction rate vs time plots for the oxidation of formic acid (2.12×10^{-2} M) by methyltributylammonium permanganate (3.00×10^{-4} M) in methylene chloride at 25.0 °C. (a) In the absence of manganese products at the beginning of the reaction. (b) In the presence of manganese products (3.00×10^{-4} M) at the beginning of the reaction. The values of the rate have been divided by four in this last case.

and the concentrations of the oxidant and the reductant. The rate of the uncatalyzed reaction is first order with respect to the concentration of permanganate (Table III) and proportional to the concentration of formic acid (Table IV). Both the catalyzed and the uncatalyzed reactions are inhibited by the presence of water (Table V).

Deuterium isotope effects for both hydrogens in formic acid were also determined. As can be seen from the data in Table VI, both reactions show a primary deuterium isotope effect for the oxidation of DCOOH but a much smaller effect for the oxidation of HCOOD.

The reactivity of formic acid toward methyltributylammonium permanganate in methylene chloride solutions has also been compared with that for the oxidation of methyl formate (Table VII). Since the kinetic order for formic acid is not exactly unity, a direct comparison of their respective rate constants is not possible. The best that can be done is to compare pseudo-first-order rate constants at a constant substrate concentration as in Table VII.

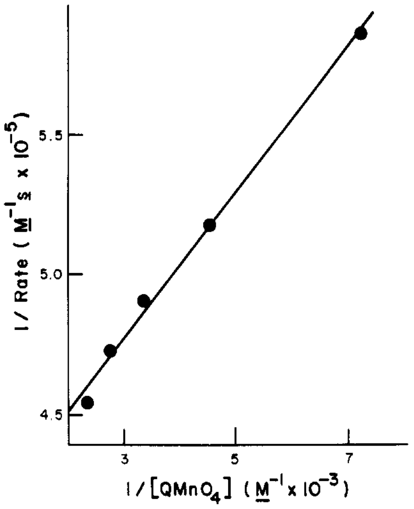


Figure 4. 1/rate$_i$ vs 1/[QMnO$_4$]$_i$ relationship for the catalytic reaction, in the presence of manganese products (3.00×10^{-4} M) at the beginning of the reaction. [HCOOH] = 2.12×10^{-2} M, T = 25.0 °C, $r = 0.998$.

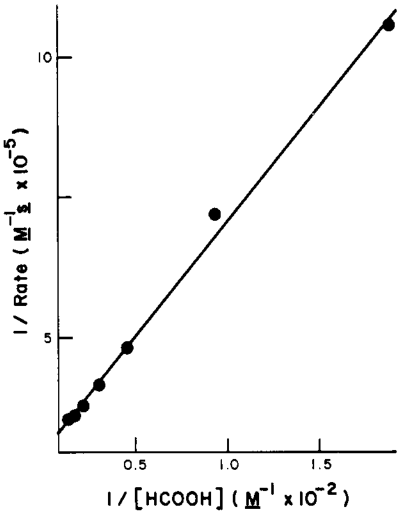


Figure 5. 1/rate$_i$ vs 1/[HCOOH] relationship for the catalyzed oxidation of formic acid by methyltributylammonium permanganate (3.00×10^{-4} M) in the presence of manganese products (3.00×10^{-4} M) at the beginning of the reaction. T = 25.0 °C, $r = 0.998$.

Table VII. Comparison of the Reactivities of Formic Acid and Methyl Formate toward Permanganate[a]

substrate	$-d[QMnO_4]/dt_i$,[b] M s^{-1}	k_1, s^{-1}
HCOOH	5.97×10^{-8}	1.99×10^{-4}
HCOOCH$_3$	1.43×10^{-10}	4.77×10^{-7}

[a] [QMnO$_4$]$_i$ = 3.00×10^{-4} M; [substrate] = 1.00×10^{-2} M; temperature = 25.0 °C; solvent = CH$_2$Cl$_2$. [b] Initial reaction state. [c] Pseudo-first-order rate constant, defined as $k_1 = (-d[QMnO_4]/dt)_i/[QMnO_4]_i$.

Discussion

The rates of autocatalytic reactions, instead of decreasing progressively as the reactants are consumed, pass through a maximum to produce bell-shaped rate vs time plots.[15] This occurs because the initial reaction (in the absence of catalytic products) is slow, but rapidly increases as the product forms, only to suffer a decline, because of depletion of the substrate, toward the end of the reaction.

In analogy with aqueous permanganate oxidations, the product that acts as a catalyst is most likely MnO_2.[10-19] Confirmation of this suggestion was obtained by comparing the rates of oxidation of formic acid in the presence of MnO_2 that had been synthesized from the photochemical reduction of permanganate[25] (Table II).

The observation that there is a linear relationship between the reciprocal for the rate of the catalyzed reaction and $1/[QMnO_4]$ may be attributed to the activation of permanganate by adsorption on the surface of MnO_2 particles, a phenomenon that has also been noted for other reactions.[20] According to the Langmuir isotherm,[26] the relationship between the amount of permanganate adsorbed, $[QMnO_4]_{ad}$, and the amount in solution, $[QMnO_4]_{sol}$, is given by eq 1.

$$[QMnO_4]_{ad} = a[QMnO_4]_{sol}/(1 + b[QMnO_4]_{sol}) \quad (1)$$

If this expression is substituted into the pseudo-first-order rate equation for this reaction, eq 2 and 3 are obtained.

$$\text{rate} = k[QMnO_4]_{ad} = ka[QMnO_4]_{sol}/(1 + b[QMnO_4]_{sol}) \quad (2)$$

$$1/\text{rate} = 1/ka[QMnO_4]_{sol} + b/ka \quad (3)$$

Consequently, it appears that activation of the oxidant by adsorption on colloidal manganese dioxide accounts, at least in part, for the autocatalysis.

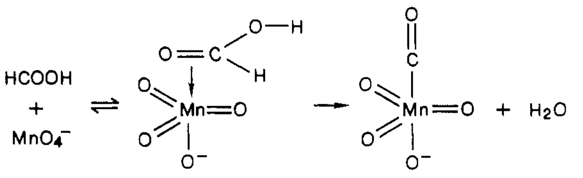
Since the rate of the catalyzed reaction bears a similar reciprocal relationship to formic acid concentration, it must also be adsorbed on the surface of the colloid at the time of reaction. In other words, the transition state must consist of an activated permanganate ion, a molecule of formic acid, and a colloidal MnO_2 particle. This mechanism would also account for the inhibition of the reaction by moisture; water would compete with the oxidant for sites available on the surface of the catalyst. The reaction could then by visualized as proceeding by way of eq 4 and 5.

$$QMnO_4 + (MnO_2)_n \rightleftharpoons QMnO_4(MnO_2)_n \quad (4)$$

$$QMnO_4(MnO_2)_n + HCO_2H \rightarrow QMnO_3(MnO_2)_n + CO_2 + H_2O \quad (5)$$

If it is assumed that reaction 5 involves a rate-limiting cleavage of the C–H bond, as previously proposed for the corresponding reaction in aqueous solutions, the isotope effects (Table VI) are quite adequately accounted for.

Since theoretical studies[27] indicate that the reactions between permanganate and organic compounds are initiated by the formation of complexes (with a concomitant increase in the coordination number of the manganese), it is quite likely that the uncatalyzed portion of the reaction would proceed as in eq 6 and 7.



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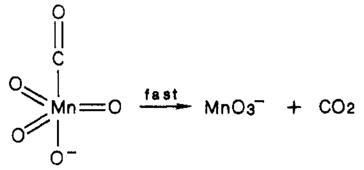

(7)

This mechanism is consistent with the observed isotope effect (Table VI) and it also accounts for the previously made observation that carbon dioxide-O^{18} is formed when permanganate-O^{18} is used as the oxidant. It further suggests that the notable reducing properties of formic acid, when compared with other carboxylic acids, may be a consequence of the ease of decarbonylation, and not the presence of a formyl group, as previously accepted.[28] If the enhanced reducing properties of formic acid were, in fact, due only to the presence of an oxidizable formyl group, it is to be expected that methyl formate (which also contains a formyl group) would be as readily oxidized. However, the oxidation of methyl formate is quite different; it shows a much diminished sensitivity to autocatalysis and a rate of reaction that is several orders of magnitude slower than the rate of oxidation of formic acid under similar conditions (Table VII).

The manganese(V) oxide formed in eq 7 would be a strong oxidant and would likely be reduced by the solvent, CH_2Cl_2, to manganese(IV), the observed product of the reaction.

The presence of water would be expected to inhibit the rate of reaction by competing with the reductant for a position in the coordination shell of manganese.

As indicated by the data in Table IV, the rate of reaction is also inhibited slightly as the concentration of formic acid in the solution increases. A 12-fold increase in concentration produces a 42% decrease in the observed second order rate constant. This may be associated with the formation of dimers as the concentration of formic acid increases.

In conclusion, it may be seen that two quite different mechanisms are required to account for the experimental observations—one for the catalytic and another for the noncatalytic portion of the reaction.

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Registry No. HCO_2H, 64-18-6; MnO_2, 1313-13-9; methyltributylammonium permanganate, 82444-42-6; deuterium, 7782-39-0.

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