Most of the kinetic studies were made with the purer nickel sample A, but even strips from sample B showed no surface formation of Al_2O_3 after extended treatment with formic acid in the kinetics apparatus. It may be that the flow of formic acid was sufficient to carry away oxygen resulting from degassing of the container walls before it came in contact with the nickel specimen. In any event, only nickel patterns were obtained by electron diffraction and the catalytic activity of the two samples with resin-treated acid was identical.

Nickel Formate Film Formation.—In view of the suggestion[8] that the decomposition of formic acid vapor on nickel may involve the intermediate formation of a nickel formate film in some instances, a study of the conditions under which such a film can develop was undertaken. Since the X-ray diffraction pattern of anhydrous nickel formate is not known, a sample was prepared from sample B nickel. In order to obtain material of suitable crystal size, nickel millings were treated with anhydrous formic acid in a Soxhlet extractor. The continuous recycling of fresh formic acid over the metal led to the gradual accumulation of crystalline product in the lower chamber of the extractor. The dried product was analyzed for carbon and hydrogen giving results in close agreement with the theoretical values for anhydrous nickel formate. The interplanar spacings from an X-ray diffraction pattern are given in Table I.

TABLE I

X-RAY PATTERN OF ANHYDROUS NICKEL FORMATE

I/I_0 Relative intensity	D_{hkl} Interplanar spacing	I/I_0 Relative intensity	D_{hkl} Interplanar spacing
s	8.47	vw	2.99
ms	8.04	m	2.86
w	7.04	m	2.79
m	6.60	m	2.62
m	4.89	m	2.55
m	4.50	w	2.423
m	4.34	w	2.362
w	4.06	vw	2.313
w	3.99	w	2.255
vw	3.80	m	2.177
vw	3.55	m	2.02
w	3.37	vw	1.945
vw	3.20	vw	1.612

Using electron microscopy and diffraction techniques, no evidence of nickel formate film formation was obtained in the temperature range in which the nickel surface shows active catalysis. However, experiments at lower temperatures between 30 and 55° showed that an anhydrous nickel formate film is produced when nickel is exposed to an atmosphere nearly saturated with formic acid. Under these conditions, multilayer adsorption of the formic acid becomes possible. Corrosion of the metal surface may then be similar to the reaction with liquid formic acid.

As an additional method for detecting the formation of a thin film, a nickel sample was suspended from one arm of the microbalance described above and its weight was followed during the course of the formic acid decomposition. At 400, 300, 200 and 50°, with 3.5 cm. pressure of formic acid vapor, no change of weight which could correspond to more than a monolayer of formic acid was observed.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BRITISH COLUMBIA]

Kinetics of the Permanganate Oxidation of Formic Acid and Formate Ion in Aqueous Solution

BY SANDRA M. TAYLOR[1] AND J. HALPERN

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The kinetics of the permanganate oxidation of formic acid in aqueous perchloric acid were examined in the temperature range 15 to 35°. The reaction, $2MnO_4^- + 3HCOOH + 2H^+ \rightarrow 2MnO_2 + 3CO_2 + 4H_2O$, appears to proceed through two independent paths in which the rate-determining steps are bimolecular reactions of permanganate with formic acid and formate ion, respectively. The kinetics are thus of the form, $-d[MnO_4^-]/dt = [MnO_4^-][HCOOH](k_1 + k_2K_i/[H^+])$. where $k_1 = 1.1 \times 10^9 \exp[-16400/RT]M^{-1}$ sec.$^{-1}$ and $k_2 = 7.8 \times 10^9 \exp[-13000/RT]M^{-1}$ sec.$^{-1}$. The formate ion reaction (k_2) exhibits a large deuterium isotope effect ($k_{HCOO^-}/k_{DCOO^-} = 7$) which suggests cleavage of the C–H bond in the rate-determining step. The absence of a corresponding isotope effect in the formic acid reaction (k_1) suggests that it proceeds by a different mechanism. A difference in mechanism for the two paths is also indicated by the observation of a considerable solvent deuterium isotope effect for k_2($k_2^{H_2O}/k_2^{D_2O} = 0.38$) but not for k_1. The reaction is susceptible to pronounced catalysis by Fe^{+++} (but not by Na^+, Ag^+, Cu^{++} or Co^{++}). The kinetics suggest that the catalytic path involves reaction of HCOOH or $HCOO^-$ with a $FeMnO_4^{++}$ complex. It seems likely that the initial reduction products of MnO_4^-, in the uncatalyzed and catalyzed reactions, are Mn(V) and Mn(VI), respectively.

Introduction

Some features of the kinetics of the permanganate oxidation of formic acid and formate salts in aqueous solution have been examined previously by Mann, Hill and Tompkins[2] and by Wiberg and Stewart.[3] In both investigations the kinetics were identified with a rate-determining reaction between permanganate and formate ion in which manganese-(V) is formed as an intermediate. Even in solutions of *p*H as low as 1.7, in which formic acid is predominantly un-ionized, there appeared to be no

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[1] Holder of a National Research Council Bursary, 1956–1957. Assistance from the National Research Council in the form of a grant-in-aid of this work is also gratefully acknowledged.

[2] D. R. Mann and F. C. Tompkins, *Trans. Faraday Soc.*, **37**, 201 (1941); L. M. Hill and F. C. Tompkins, *Trans. Roy. Soc. S. Africa*, **29**, 309 (1942); **30**, 59 (1943).

[3] K. B. Wiberg and R. Stewart, THIS JOURNAL, **78**, 1214 (1956).

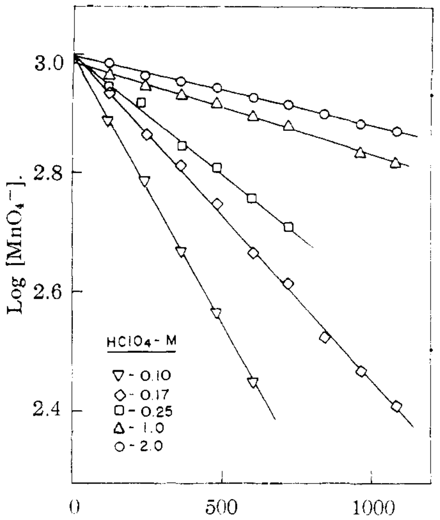

Fig. 1.—Typical rate plots for the permanganate oxidation of formic acid at 30.1°. HCOOH concn. = 0.1 *M*; ionic strength adjusted to 2.0 with $NaClO_4$.

contribution from a parallel path involving direct reaction between permanganate and un-ionized formic acid molecules. In the present investigation kinetic measurements were extended to solutions of higher acidity (up to 2 *M* H^+) with a view to establishing the existence and kinetics of this path. Further insight into the mechanism of this and related reactions was sought through (i) measurements of the reactant- and solvent-deuterium kinetic isotope effects and (ii) examination of the catalytic effects of metal ions.

Experimental

Solutions were prepared from reagent grade chemicals and distilled water. Formic acid was redistilled twice before use. Deuteriated formic acids (DCOOD and DCOOH) of isotopic purity[4] exceeding 98% were prepared by the method described by Wiberg and Stewart.[3] A solution of $DClO_4$ in D_2O was prepared by five successive equilibrations of 165 g. of 70% $HClO_4$ with 30-ml. portions of D_2O (obtained from Stuart Oxygen Co.), excess water being removed after each equilibration by distillation under reduced pressure. Dilution with D_2O to 1 *M* $DClO_4$ (the highest concentration used in the kinetic experiments) gave a solution of isotopic purity exceeding 98%.

The kinetic measurements were made by quenching aliquot samples of the reaction mixture (including the precipitated MnO_2 product) with a known excess of potassium iodide and titrating the liberated iodine with thiosulfate. The samples were contained in separate brown bottles, thermostated to 0.05°. To minimize the zero-time error the reaction in each bottle was started by rapid mixing of solutions of the two reactants, each having been previously brought to the reaction temperature.

The ionization constants of DCOOH and HCOOH were determined in 1 *M* $NaClO_4$ solutions by measuring the *p*H of solutions of known concentrations (generally ranging from 0.05 to 0.2 *M* in each) of HCOOH and $HCOO^-$ (or DCOOH and $DCOO^-$) with a Beckman Model G *p*H meter.

Results and Discussion

It was established, in agreement with earlier observations,[2,3] that the stoichiometry of the reaction conforms to

$$2MnO_4^- + 3HCOOH + 2H^+ \longrightarrow 2MnO_2 + 3CO_2 + 4H_2O \quad (1)$$

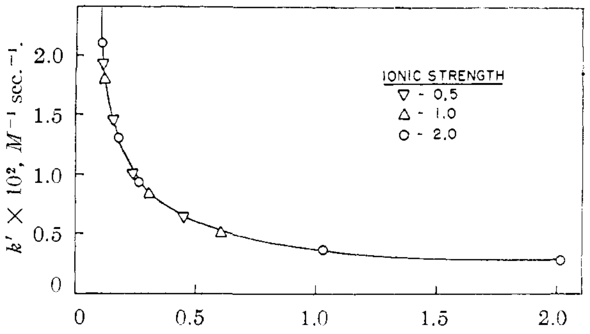

Fig. 2.—Dependence of *k'* on [H^+] at 30.1°.

Under the conditions examined, oxidation of HCOOH by MnO_2 was much slower than by MnO_4^- and could be neglected until reaction 1 had proceeded to the extent of at least 50%. The reaction was unaffected by exposure to light and by the addition of glass wool.

Kinetics of the Reaction.—At constant $HClO_4$ concentration the kinetics of reaction 1 were found to be of the form

$$-d[MnO_4^-]/dt = k'[MnO_4^-][HCOOH] \quad (2)$$

Most of the experiments were made with the HCOOH concentration in considerable excess over that of MnO_4^- and values of *k'* were determined from the slopes of pseudo first-order plots, typical examples of which are shown in Fig. 1. *k'* was found to depend inversely on the H^+ concentration but showed a tendency to approach a finite limiting value when the latter was increased beyond 1 *M* (Fig. 2). It seems likely that this represents the rate constant for the reaction of MnO_4^- with un-ionized HCOOH, while the increase in *k'* with decreasing H^+ is due to contributions from reaction with $HCOO^-$, the latter species being the more reactive. The assumption that the two species react independently with MnO_4^- leads to the rate law

$$-d[MnO_4^-]/dt = k_1[HCOOH][MnO_4^-] + k_2[HCOO^-][MnO_4^-] \quad (3)$$

$$= (k_1 + k_2K_i/[H^+])[HCOOH][MnO_4^-] \quad (4)$$

where K_i is the ionization constant of formic acid. In acid solutions formic acid is predominantly un-ionized and hence [HCOOH] may be approximated by the total formic acid concentration. Comparison of equations 1 and 4 thus yields the relation

$$k' = k_1 + k_2K_i/[H^+] \quad (5)$$

in accord with the linear plots of *k'* *vs.* $1/[H^+]$ shown in Fig. 3.

An earlier investigation by Mann and Tompkins[2] of the *p*H-dependence of the rate of the permanganate oxidation of formic acid was confined to solutions of *p*H exceeding 1.7. In this region, as is evident from Fig. 3, the first term in equation 3 and 4 corresponding to the contribution of un-ionized HCOOH to the reaction, is relatively small and hence was not detected.

Neither k_1 nor k_2K_i was affected when the ionic strength of the solution was varied (by adjustment

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[4] We are indebted to T. M. Connor for determining the n.m.r. spectra on which these estimates of isotopic purity are based.

of the $NaClO_4$ concentration) between 0.5 and 2.0 *M* (Fig. 2). At lower ionic strengths (below 0.1 *M*) k_2 was observed by Hill and Tompkins[2] to increase with ionic strength in accord with the predictions of the Debye–Huckel theory. However the present measurements, of necessity, lie far outside the Debye–Huckel region, covering a range over which the activity coefficients of many electrolytes are known[5] to be fairly independent of ionic strength.

Values of k_1 and k_2K_i for various temperatures ranging from 15.6 to 35.0°, corresponding to the intercepts and slopes of the plots in Fig. 3 are listed in Table I. These measurements refer to solutions of ionic strength = 1 and K_i correspondingly was also determined at this ionic strength. Its value at 30° was found to be 5.6×10^{-4} *M*. In line with Harned's findings that the heats of ionization of formic acid[6] and other carboxylic acids[7] are close to zero in the vicinity of 25°, this value was assumed for the whole temperature range (15 to 35°) covered by the kinetic measurements and used to compute the values of k_2 listed in Table I.

TABLE I

RATE CONSTANTS AT VARIOUS TEMPERATURES

Temp., °C.	$k_1 \times 10^3$, M^{-1} sec.$^{-1}$	$k_2K_i \times 10^3$, sec.$^{-1}$	k_2, M^{-1} sec.$^{-1}$
15.6	0.45	0.72	1.28
22.8	0.88	1.22	1.57
25.8	1.15	1.59	2.09
30.1	1.70	1.95	3.48
32.7	2.15	2.47	4.41
35.0	2.60	2.87	5.09

Both k_1 and k_2 gave good Arrhenius plots, fitted, respectively, by the equations

$$k_1 = 1.1 \times 10^9 \exp[-16400/RT]\ M^{-1}\ \text{sec.}^{-1} \quad (6)$$

and

$$k_2 = 7.8 \times 10^9 \exp[-13000/RT]\ M^{-1}\ \text{sec.}^{-1} \quad (7)$$

The corresponding entropies of activation are $\Delta S_1^{\ddagger} = -19$ e.u. and $\Delta S_2^{\ddagger} = -15$ e.u. The above values for the activation energy and entropy of the formate ion reaction are in reasonable agreement with those ($E_2 = 11.9$ kcal./mole; $\Delta S_2^{\ddagger} = -21$ e.u.) found by Hill and Tompkins[2] at an ionic strength of 0.084, particularly in the light of their observation that both these values tend to increase with ionic strength. E_1 and $\Delta S_1^{\ddagger}$ have not been previously determined.

Deuterium Isotope Effects.—In addition to the $HCOOH-H_2O-HClO_4$ system described above, the kinetics of the reaction were examined at 29.9° in the isotopically related systems listed in Table II in which reactant and/or solvent hydrogen was substituted by deuterium. Rate constants were determined for each system from the intercepts and slopes of linear plots of k' *vs.* $[H^+]^{-1}$ (or $[D^+]^{-1}$) and these together with the values of K_i used in the computation of k_2 are listed in Table II. The values of K_i for HCOOH and DCOOH in H_2O were determined experimentally. Those for the corresponding acids in D_2O are derived from these values through the relation, $K_i(D_2O)/K_i(H_2O) = 0.34$. This corresponds to the ratio of the ionization constants of formic acid in D_2O and H_2O determined by Orr and Butler[8] and to the general relation between the ionization constants of weak acids in the two media, found by Martin and Butler[9] and by Rule and LaMer.[10]

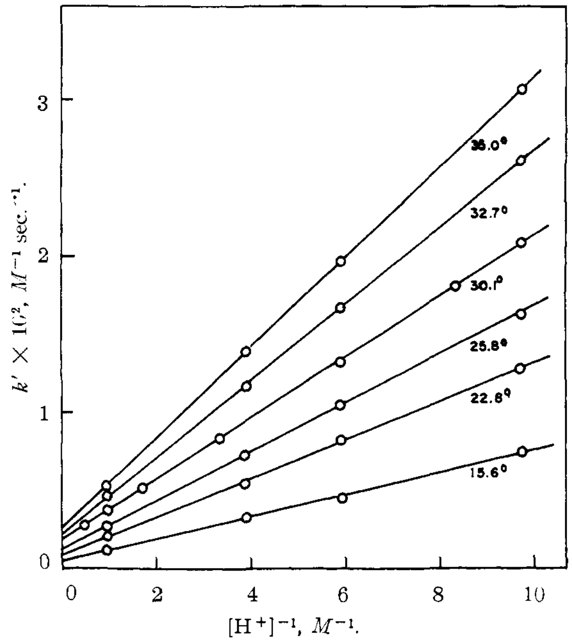

Fig. 3.—Dependence of k' on $1/[H^+]$ at various temperatures.

TABLE II

IONIZATION AND RATE CONSTANTS FOR VARIOUS ISOTOPIC SYSTEMS

(T = 29.9°; μ = 1)

Isotopic system	$K_i \times 10^4$, *M*	$k_1 \times 10^3$, M^{-1} sec.$^{-1}$	k_2, M^{-1} sec.$^{-1}$
$HCOOH-H_2O-HClO_4$	5.6	1.69	3.5
$DCOOH-H_2O-HClO_4$	8.0	1.60	0.59
$HCOOD-D_2O-DClO_4$	1.9	1.50	9.1
$DCOOD-D_2O-DlCO_4$	2.7	1.57	1.3

The following is a summary of the observed isotope effects

(a) Reactant isotope effects

$(k_1^{HCOOH}/k_1^{DCOOH})_{H_2O} = 1.06 \qquad (k_2^{HCOO^-}/k_2^{DCOO^-})_{H_2O} = 7.0$

$(k_1^{HCOOD}/k_1^{DCOOD})_{D_2O} = 0.96 \qquad (k_2^{HCOO^-}/k_2^{DHOO^-})_{D_2O} = 7.0$

(b) Solvent isotope effects

$(k_1^{H_2O}/k_1^{D_2O})_{HCOOH} = 1.13 \qquad (k_2^{H_2O}/k_2^{D_2O})_{HCOO^-} = 0.38$

$(k_1^{H_2O}/k_1^{D_2O})_{DCOOH} = 1.02 \qquad (k_2^{H_2O}/k_2^{D_2O})_{DCOO^-} = 0.38$

Both in H_2O and D_2O, k_2 for $HCOO^-$ was found to be about 7 times as large as for $DCOO^-$, in agreement with the earlier findings of Wiberg and Stewart[3] and of Aebi, Buser and Lüthi.[11] Furthermore k_2 is considerably greater in D_2O than in H_2O. In contrast, k_1 does not exhibit either an appreciable reactant or solvent isotope effect.

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(5) B. E. Conway, "Electrochemical Data," Elsevier Publishing Co., Amsterdam, 1952, pp. 75–81.

(6) H. S. Harned and N. D. Embree, THIS JOURNAL, **56**, 1042 (1934).

(7) H. S. Harned and R. W. Ehlers, *ibid.*, **55**, 652, 2379 (1933).

(8) W. J. C. Orr and J. A. V. Butler, *J. Chem. Soc.*, 33 (1937).

(9) D. C. Martin and J. A. V. Butler, *ibid.*, 1366 (1939).

(10) C. K. Rule and V. K. LaMer, THIS JOURNAL, **60**, 1974 (1938).

(11) H. Aebi, W. Buser and Chr. Lüthi, *Helv. Chim. Acta*, **39**, 944 (1956).

Catalysis by Fe^{+++}.—In view of the pronounced effect which Ag^+ has recently been shown[12] to have on the related permanganate oxidation of molecular hydrogen, it was considered of interest to examine the possible catalytic effects of this and other metal ions on the present reaction. At 30°, the rate in 1 M $HClO_4$ solution was found to be unaffected by the addition of up to 0.01 M each of Ag^+ Cu^{++} or Co^{++}(all as their perchlorate salts). On the other hand a pronounced catalytic effect was observed for Fe^{+++}.

The dependence of the rate on the Fe^{+++} concentration is depicted in Fig. 4. The apparent rate constant, k'', is defined by the rate law

$$-d[MnO_4^-]/dt = k''[MnO_4^-][HCOOH] \quad (8)$$

and thus includes contributions from both the uncatalyzed and catalyzed paths.

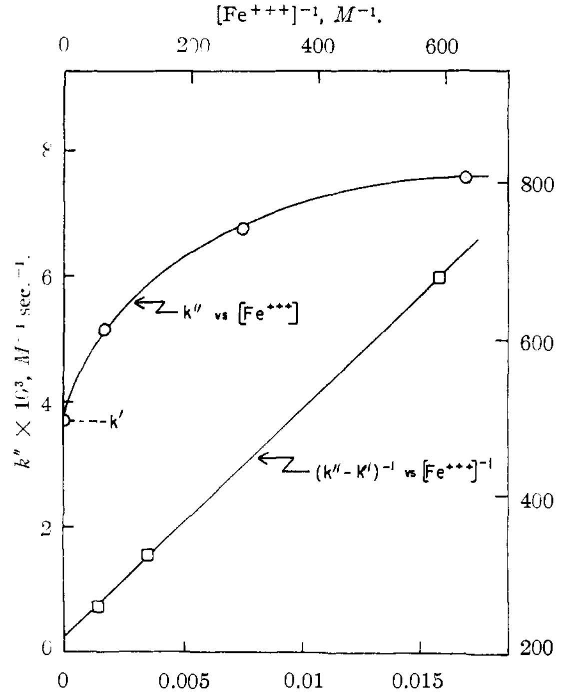

Fig. 4.—Catalysis of the reaction by Fe^{+++}; $T = 29.9°$; $HClO_4 = 1.2\ M$.

It was established that under the conditions of these experiments the oxidation of HCOOH by Fe^{+++} is negligibly slow so that a catalytic mechanism involving such a step followed by reoxidation of Fe^{++} by MnO_4^- appears ruled out. The form of the kinetics and, in particular, the tendency of the rate to level off and approach a limiting value as the Fe^{+++} concentration is increased (Fig. 4) rather suggests that the catalysis may be due to oxidation of HCOOH by a Fe^{+++}–MnO_4^- complex or ion-pair which is formed in a rapid pre-equilibrium

$$Fe^{+++} + MnO_4^- \rightleftharpoons FeMnO_4^{++} \quad (9)$$

governed by the equilibrium constant K. This would result in a rate law of the form

$$-d[MnO_4^-]/dt = k'[HCOOH][MnO_4^-] + k_c[HCOOH][FeMnO_4^{++}] \quad (10)$$

By introducing the relations

$$[MnO_4^-]_T = [MnO_4^-] + [FeMnO_4^{++}] \quad (11)$$

where $[MnO_4^-]_T$ is the total permanganate concentration, and

$$[FeMnO_4^{++}]/[Fe^{+++}][MnO_4^-] = K \quad (12)$$

this may be converted to the form

$$\frac{-d[MnO_4^-]}{dt} = \left\{k' + \frac{(k_c - k')K[Fe^{+++}]}{1 + K[Fe^{+++}]}\right\}[HCOOH][MnO_4^-]_T \quad (13)$$

whence

$$k'' = k' + (k_c - k')K[Fe^{+++}]/(1 + K[Fe^{+++}]) \quad (14)$$

This is consistent with the linear plot of $(k'' - k')^{-1}$ *vs.* $[Fe^{+++}]^{-1}$ in Fig. 4, whose slope and intercept yield values of $k_c = 8.4 \times 10^{-3} M^{-1} sec.^{-1}$ and $K = 273\ M^{-1}$, the measured value of k' being $3.7 \times 10^{-3} M^{-1} sec.^{-1}$.

No attempt was made to establish the *p*H-dependence of the catalyzed reaction or to determine the relative contributions of HCOOH and $HCOO^-$ to this reaction. If both species contribute, then k_c (like k') will be a composite function of two rate constants and of the H^+ concentration.

It should be emphasized that while the above interpretation of the catalytic effect of Fe^{+++} is in convincing accord with the kinetic results, there does not appear to be any direct corroborative evidence for the existence of the proposed $FeMnO_4^{++}$ complex.

Mechanism of the Reaction.—Earlier workers[2,3] have proposed that the rate-determining step in the permanganate oxidation of formate ion involves a two-equivalent reduction of permanganate leading to the formation of Mn(V) as an intermediate. (The alternative possibility of an initial one-equivalent reduction is much less probable on energetic grounds and this conclusion applies also to the uncatalyzed permanganate–formic acid reaction.) There are several possible types of mechanisms by which this may be accomplished, of which the following represent some of the more obvious limiting cases

(A) Hydride ion transfer from formate to permanganate

$$HCO_2^- + MnO_4^- \longrightarrow CO_2 + HMnO_4^=$$

(B) Transfer of two electrons from formate to permanganate (possibly coupled with proton transfer to a water molecule)

$$HCO_2^- + MnO_4^- \longrightarrow HCO_2^+ \text{ (or } H^+ + CO_2) + MnO_4^=$$

(C) Transfer of an oxygen atom from permanganate to formate

$$HCO_2^- + MnO_4^- \longrightarrow HCO_3^- + MnO_3^-$$

Wiberg and Stewart[3] have considered the mechanism of the formate ion–permanganate reaction in some detail and have pointed out that neither mechanism A nor C alone (this would apply also to B) explain *both* the large deuterium isotope effect *and* their observation (based on experiments using O^{18}-labeled permanganate) that a considerable proportion of the oxygen in the CO_2 product comes from the permanganate. They considered several more complex mechanisms involving simultaneous hydrogen and oxygen shifts, as well as the possibility that more than one reaction path may be involved. However, the evidence required for a

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[12] A. H. Webster and J. Halpern, *Trans. Faraday Soc.*, **53**, 51 (1957).

critical assessment of these various possibilities appears to be lacking. The present investigation adds the further knowledge that the reaction is subject to a rather large medium (H_2O–D_2O) kinetic isotope effect but an unequivocal mechanistic interpretation of this as well as the features noted above still does not seem possible.

Perhaps of greatest interest in connection with the present investigation is the comparison of the $HCOO^-$ and HCOOH reaction paths. Rate determining steps analogous to (A), (B) and (C) can be written also for HCOOH, and for this reaction also it may be concluded that the initial reduction product of MnO_4^- is Mn(V). In comparing the two reaction paths the following points appear particularly significant.

1. The rate of reaction of $HCOO^-$ with MnO_4^- exceeds that of HCOOH by a factor of more than 10^3. This is somewhat surprising since electrostatic considerations would tend to favor the reverse order, if both species reacted through the same mechanism.[13]

2. Differences in the activation energy and entropy are in the same direction and both contribute to the observed rate difference. The order of the activation entropies is unexpected, the entropy of the anion–anion reaction being less negative (−15 *vs.* −19 e.u.) than that for the anion–neutral molecule reaction. The former value seems normal while the latter is abnormally negative. In this connection it is of interest that the activation entropy (−17 e.u.) of the related reaction between MnO_4^- and H_2 (which also involves initial reduction of MnO_4^- to Mn(V)) is also abnormally negative. In both cases this could reflect increased charge separation in the activated complex resulting from transfer of negative charge (electrons or a hydride ion) from H_2 or HCOOH to MnO_4^-.

3. Further powerful evidence that HCOOH and $HCOO^-$ react by different mechanisms is provided by the different deuterium isotope effects observed for the two reactions. The absence of an isotope effect in the former case appears to rule out a mechanism involving hydride ion or proton transfer as the rate-determining process. Alternative possibilities are electron transfer from HCOOH to MnO_4^- or oxygen atom transfer in the opposite direction. Unfortunately it is not possible (because CO_2 exchanges oxygen rapidly with H_2O under acidic conditions) to test for oxygen transfer by tracer methods.

4. The manifestation of a solvent (H_2O–D_2O) isotope effect in the $HCOO^-$ reaction and its absence in the HCOOH reaction may also be related to the difference in reaction mechanism. Alternatively a "medium" effect (*e.g.*, reflecting differences in the solvating properties of H_2O and D_2O) might be involved which is important in the reaction between two ions but not in that between an ion and a neutral molecule. This question is of considerable interest in view of recent studies of solvent isotope effects in other oxidation–reduction reactions[14] and of the uncertainties connected with the interpretation of the results in most such systems.

The catalysis of the reaction by Fe^{+++} is believed to involve a path in which Mn(VI) rather than Mn(V) is formed as the initial reduction product. This corresponds to a rate-determining step whose stoichiometry is represented by

$$FeMnO_4^{++} + HCOOH \longrightarrow Fe^{++} + MnO_4^- + CO_2 + 2H^+ \tag{15}$$

(or by a similar reaction involving $HCOO^-$). This interpretation is very similar to that proposed[12] for the catalytic effect of Ag^+ in the reaction of MnO_4^- with H_2 and in each case the catalytic function of the metal ion is related to its tendency to undergo reversible one-electron reduction (and possibly also to its tendency to complex with permanganate). In view of the close analogy between the two systems, the apparent absence of reciprocal catalytic effects (*i.e.*, catalysis of the MnO_4^--HCOOH reaction by Ag^+ and of the MnO_4^--H_2 reaction by Fe^{+++}) is somewhat surprising and remains to be explained.

VANCOUVER, B. C., CANADA

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[13] A suggestion in this connection, made by the referee, is that the very stable carbon dioxide structure provides a driving force for the reaction of $HCOO^-$ by hydride transfer which does not contribute to the reaction of HCOOH.

[14] J. Hudis and R. W. Dodson, THIS JOURNAL, **78**, 911 (1956); F. B. Baker and T. W. Newton, *J. Phys. Chem.*, **61**, 381 (1957); A. E. Ogard and H. Taube, THIS JOURNAL, **80**, 1084 (1958); T. W. Newton and S. W. Rabideau, *J. Phys. Chem.*, **63**, 365 (1959).