

KINETICS OF THE OXIDATION OF HCOOH WITH KMnO_4 OVER A WIDE RANGE OF pH

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ABSTRACT

Kinetics of the chemical oxidation of HCOOH with KMnO_4 has been studied over a wide range of pH (2-7). The effect of pH on the apparent rate constant of the redox reaction shows unexpected behavior with a maximum located between pH 4 and 5. The order with respect to KMnO_4 and HCOOH was found to be one and a half, respectively. The effect of the ionic strength suggests that the reaction occurs rather between HCOO^- and MnO_4^- even at pH lower than the pK_a of HCOOH. The thermodynamic parameters were also calculated at several pH values. The free activation energy is independent of pH, so perhaps, the oxidation occurred via several steps, but the transient species is the same at any pH.

***Keywords:** oxidation, formic acid, order of reaction, effect of pH, effect of ionic strength, thermodynamic parameters.*

INTRODUCTION

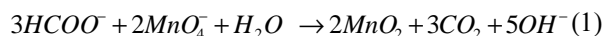
The first carboxylic acids are H-COOH, $\text{CH}_3\text{-COOH}$ and HOOC-COOH. Formic acid is a byproduct of the degradation of organic pollutant compounds used in industry [1]. It is also a byproduct of the oxidation of maleic acid which is an intermediate in the degradation of the aromatic ring [2]. Formic acid has a simple structure and only two electrons in its oxidation to CO_2 , but its oxidation mechanism (via chemical or electrochemical way) has been found to be rather complex [3, 4]. Aqueous solutions of formic acid and methanol represent two potential, attractive energy sources for fuel cells [5]. Thus, a great deal of research effort has been focused on the electrochemical properties of formic acid, which serves as an important model system for studying electrochemical oxidation of small organic molecules [6-8]

Many articles have treated the kinetics of the oxidation of formic acid with different oxidants such as KMnO_4 [3, 9], Br_2 [10-12] and Bi(V) [13].

The kinetic of the oxidation of formic acid by Br_2 in aqueous solution showed that the acidity affects the rate and the reaction occurs on its anion [11]. α -Cyclodextrin modestly increases the oxidation rate of formic acid by Br_2 [12]. Kinetic and mechanism studies of oxidation of HCOOH with chloramine-T in aqueous acidic medium showed that the oxidation occurs via two ways and the reaction rate is retarded by one of the reaction products [14]. Studying the kinetics and the mechanism of the oxidation of HCOOH by bis - (2,2'-bipyridil)Cu(II) permanganate (BBCP) showed that the order with respect to formic acid is less than one in the absence of HClO_4 , whereas in its presence, the order is between one and two [15].

The kinetics of the permanganate oxidations of formic acid have been extensively studied in the last decades [3], but several discrepancies were observed. The results of the latest articles indicated that this reaction is autocatalyzed by both Mn(II) and colloidal MnO₂ (formed as an intermediate) [9] and proceeds via several parallel reactions, undergoing the same transient acidic species HCO₂⁺ [3]. This study also introduced two new terms to the rate equation. These terms are related to the MnO₄⁻ autocatalytic effect and acid media inhibition effect.

pH effect arises when one of the reagents has acid-base property, affecting the reactivity of that reagent such as the slow oxidation of formic acid by permanganate:



The kinetics of the oxidation of formic acid is done at pH ≤ 1 in most of the articles mentioned before. Few literatures references spoke about the chemical oxidation of HCOOH over a large pH range. The effect of pH on the reaction of HCOOH with KMnO₄ was studied at only two pH values (3.6 and 6.6) [16]. They suggested specific acid catalysis and negligible action of the ionic strength.

In this paper, a full kinetic study of the oxidation of formic acid with KMnO₄ in function of pH was investigated to fill this gap and the corresponding thermodynamics parameters are also calculated. KMnO₄ is selected since it is a well known oxidant used in organic chemistry to oxidize small and large biological molecules [17,18].

EXPERIMENTAL

All chemicals used were analytical reagent grade. 0.015 M KMnO₄ mother solution was prepared weekly and stored in an amber bottle. The concentration of formic acid used was 0.2 M. H₃PO₄, KH₂PO₄ and Na₂HPO₄ solutions of the same concentration (0.04 M) are used in different proportions to fix the pH of the solution at the desired value. Phosphate buffer is selected since it delays the precipitation of MnO₂ by adsorption of phosphate ions on their surface [19] and so allows better measurement of the absorbance. In absence of any com-

pound preventing the precipitation of MnO₂, kinetic study is impossible.

KMnO₄ has two maxima in the visible region (of the same intensity) at 524 nm and 545 nm [16]. HCOOH is colorless so the absorbance at 545 nm was selected to follow the kinetics of the reaction, because at this wavelength, we have less interference from soluble form of MnO₂ (brown) since its spectrum overlaps the permanganate bands more at 524 nm.

The kinetic study as a function of pH was carried on a double beam spectrophotometer, Specord 200 (analytical Jena). The desired pH was obtained by varying the percentage of phosphate solutions as mentioned above, and measured with a combined glass electrode.

The order with respect to the two reactants was determined: The order with respect to KMnO₄ is done in presence of constant excess of the formic acid, whereas the order with respect to formic acid was obtained in presence of different excess of it in the reactional mixture ranging from 0.011 M to 0.034 M. The reactional mixture is obtained as follows: 10 ml of 15 × 10⁻⁴ M KMnO₄ (obtained by dilution) was added quickly to the stirred mixture already prepared (40 ml of 0.04 M phosphate buffer, 5 ml of 0.2 M HCOOH and 10 ml of 1 M of appropriate strong electrolyte such as NaNO₃). Quickly after the addition of KMnO₄, the absorbance was recorded after each 10 s for 8 minutes.

A kinetic study as a function of temperature (13 - 35°C) was carried out, also at several pH, to determine the activation parameters (E_a , ΔH^\ddagger , ΔS^\ddagger , ΔG^\ddagger).

RESULTS AND DISCUSSION

The determination of the pseudo order of the reaction with respect to KMnO₄ was done with or without fixing the ionic strength. Time versus absorbance (at 545 nm) profile showed an exponential decay in absorbance with an increase in time, in contrast to the variation of A₅₄₅ vs. time in presence of oxalic acid which is influenced by the initial added concentration of Mn(II) (Fig. 1). As the curves obtained are sigmoidal, we can say that we are in front of autocatalytic reaction by Mn(II) [20]. Fig. 1 shows also that the initial concentration of Mn(II) affects strongly the time corresponding to the high rate but has little effect on the shape of the curve.

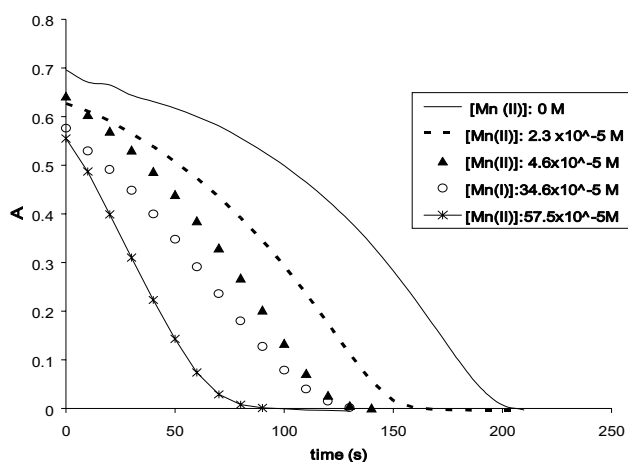


Fig. 1. Effect of Mn (II) concentration on the reaction of oxalic acid with KMnO_4 (at 20°C , pH 1). $[\text{KMnO}_4]$: 1.5×10^{-4} M, $[\text{oxalic acid}]$: 0.014 M.

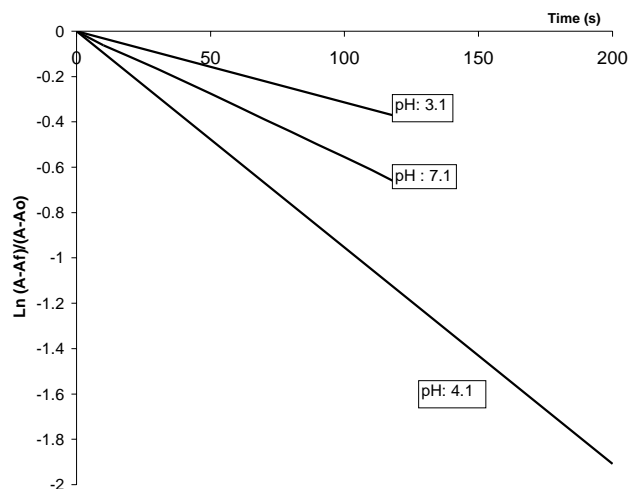


Fig. 2. Order of the reaction with respect to KMnO_4 at several pH. $[\text{HCOOH}]$ 0.014 M, $[\text{KMnO}_4]$ 2.14×10^{-4} M, 0.14 M NaNO_3 .

The apparent constant (k_{app}) was calculated by slope value of linear best fit equation of time versus $\ln \frac{[\text{MnO}_4^-]}{[\text{MnO}_4^-]_0} = \ln \frac{(A - A_\infty)}{(A_0 - A_\infty)}$, where A is the absorbance at time t (A_{545}), A_∞ is the final absorbance (due to $\text{MnO}_{2(aq)}$) and A_0 is the initial absorbance [16]. The order zero is rejected since the plot A_{545} vs. time showed an exponential decay. The order remains 1 over a range of pH 2-8 (Fig. 2). Successive scans at 30 s intervals during the reaction in phosphate buffer showed an isosbestic point at 460 nm (Fig. 3) which reinforces the idea about the solubility of colloid MnO_2 as mentioned by Benito [19]. In accordance with this, the absorbance obeys to

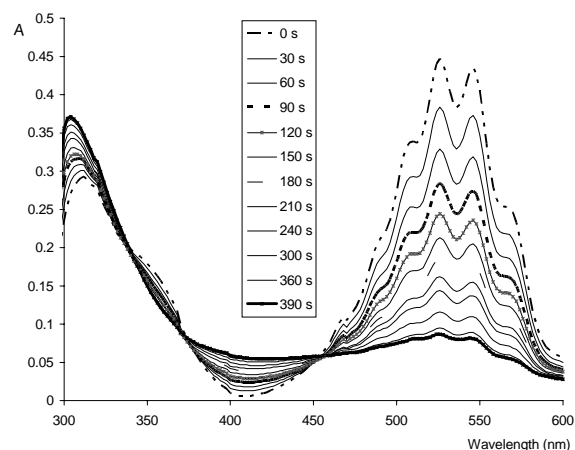


Fig. 3. Evolution of the spectra of the mixture $\text{KMnO}_4 + \text{HCOOH}$ in function of time, T 18°C and pH 2.8. $[\text{HCOOH}]$ 0.014 M, $[\text{KMnO}_4]$ 2.14×10^{-4} M, 0.14 M NaNO_3 .

Beer's law, since A_{545} or A_{525} vs. A_{418} (proportional to $[\text{MnO}_{2(aq)}]$) plot is linear (R^2 0.998). The spectra of the same mixture under the same conditions, but without phosphate buffer, does not show any isosbestic point, and further more these spectra are not exploited.

The kinetic study at several excess of HCOOH, allows finding the order with respect to HCOOH. The slope of the line obtained by drawing $\ln V_i$ (or $\ln k_{app}$) vs. $\ln [\text{HCOOH}]$ corresponds to the order with respect to HCOOH (V_i - initial rate). This study is done at several pH values (2.3, 4.2 and 6.3). The initial rate of the reaction increases with the increase of the HCOOH excess. At these pH values, the order with respect to HCOOH is 0.5 (with R^2 0.997) (Fig. 4).

In some cases the rate of a chemical reaction is affected by the presence of salt in solution (salt effect). The electrochemical oxidation of uric acid in phosphate buffer in variable ionic strength is good example of primary salt effect [21]. The results obtained by Banerji showed that the oxidation of HCOOH by BBCP is not sensitive to changes in ionic strength (I) [15], but in this study, preliminary experiments showed that the rate constant (k_{app}) increases with the increase in the concentration of KH_2PO_4 buffer in solution (pH ~ 3). The apparent rate constant also increases by a factor 1.5 in presence of 10 ml of 1 M Na_2SO_4 in the mixture (Fig. 5). Hence, to confirm the effect of the ionic strength on k_{app} , a kinetic study was done at several (I) values ranging from 0.015 to 0.45. The results showed that k_{app} varies linearly with the ionic strength (I) according to the empirical Davies equation in aqueous solution [22]:

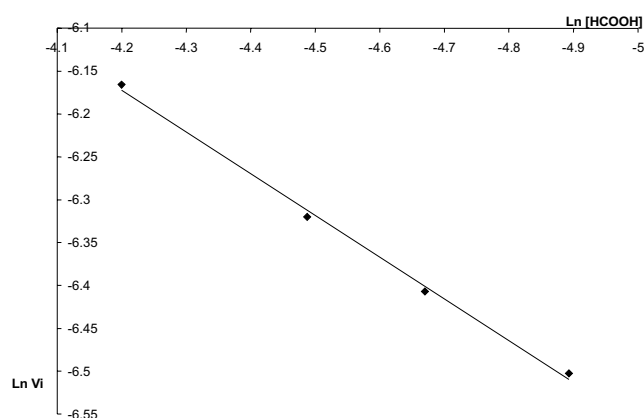


Fig. 4. Order of the reaction with respect to HCOOH (pH 6.4) $[KMnO_4] 2.14 \times 10^{-4} M$, variable excess of $[HCOOH]$, V_i - initial rate.

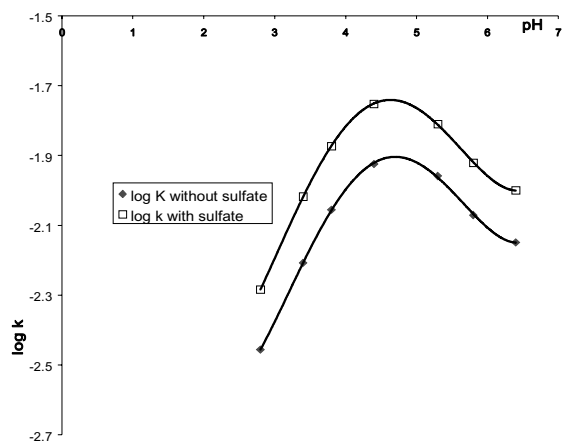


Fig. 5. Effect of pH on the rate constant (k_{app}) of the oxidation of HCOOH with $KMnO_4$. $[HCOOH] 0.014 M$, $[KMnO_4] 2.14 \times 10^{-4} M$, $0.14 M Na_2SO_4$.

$$\log k_{app} = \log k_{o,app} + Z_a \times Z_b \times \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2 \times I \right)$$

for $I < 0.5 M$ (2)

where: Z_a and Z_b - charges on ions A and B;
 k_{app} and $k_{o,app}$ - rate constants at ionic strength different from zero and at $I = 0$, respectively.

In Davies equation, there is a new term $(0.2 I)$ with respect to Brønsted equation. It was found that a

$$\log k_{app} \text{ versus } \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2 \times I \right) \text{ or } \left(\frac{\sqrt{I}}{\sqrt{I+1}} \right)$$

plot exhibited a straight line with a positive slope ~ 1 as shown in Fig. 6. It can be concluded that the reaction

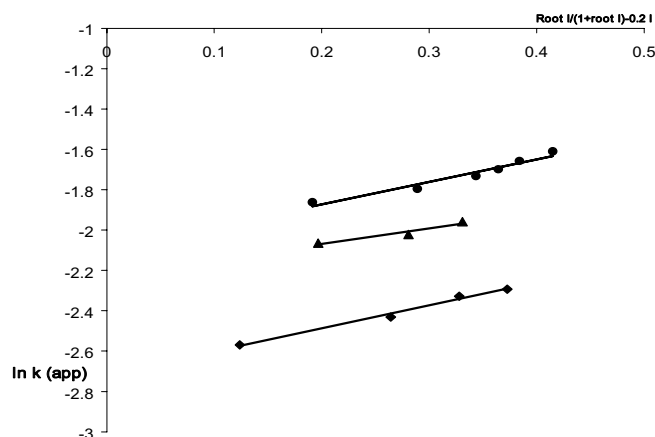


Fig. 6. Variation of $\log k_{app}$ vs. $(\sqrt{I}/(1 + \sqrt{I}) - 0.2I)$ at different pH. pH 5, 6.3 and 2.8, $T 19^\circ C$, in presence of variable $[Na_2SO_4]$. $[HCOOH] 0.014 M$, $[KMnO_4] 2.14 \times 10^{-4} M$.

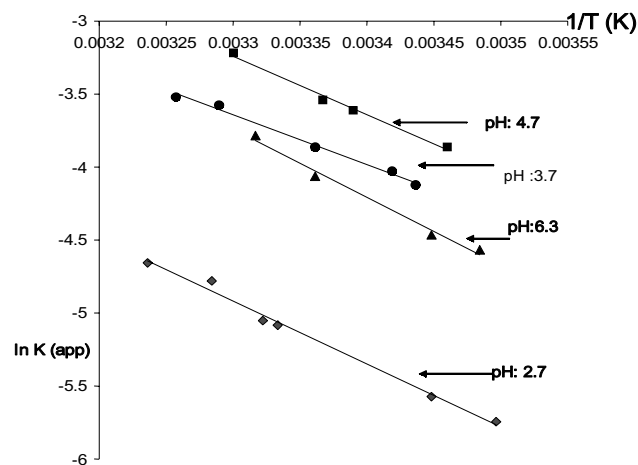


Fig. 7. Arrhenius plot of $\ln k_{app}$ vs. $1/T$ at several pH. $[HCOOH] 0.014 M$, $[KMnO_4] 2.14 \times 10^{-4} M$, $0.14 M NaNO_3$.

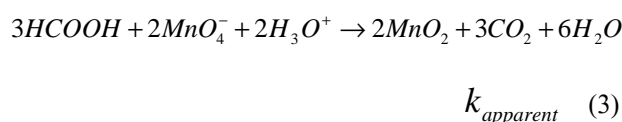
probably occurred with the base $HCOO^-$ and not with $HCOOH$. Since the rate constant varies with the ionic strength, the study of the pH effect was done in presence of 10 ml of 1M Na_2SO_4 to keep the ionic strength constant.

The standard potentials of the two systems MnO_4^-/MnO_2 and $HCOOH/CO_2$ are function of pH [16]. $KMnO_4$ belongs to complex redox system, it can be reduced to $Mn(II)$ in acidic medium or to MnO_2 for pH higher than 2. $HCOOH$ or $HCOO^-$ can be oxidized to CO_2 (or to HCO_3^- for $pH > 6$). E° of $HCOOH/CO_2$ is $-0.114 V$ and E° of MnO_4^-/MnO_2 is $1.69 V$ at pH zero [23]. According to δ rule, the equilibrium constant of the redox reaction is very high ($\sim 10^{180}$), but the reac-

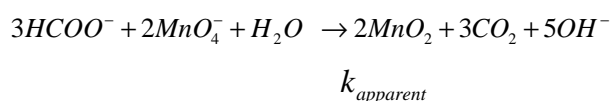
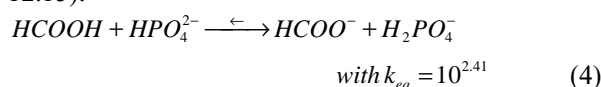
Table1: Thermodynamic parameters of the oxidation of HCOOH with KMnO₄ at several pH (ΔG^\ddagger is calculated at 298 K).

pH	E _a (kJ.mol ⁻¹)	ΔH^\ddagger (kJ.mol ⁻¹)	ΔS^\ddagger (J/mol.K)	ΔG^\ddagger (kJ.mol ⁻¹)
2.7	36	33	-177	86
3.7	28	26	-190	83
4.7	33	31	-170	82
6.3	39	36	-156	82

tion is slow kinetically. For pH less than pKa of HCOOH (3.8), we have for irreversible slow reaction:



For pH higher than pKa, HCOOH reacts quantitatively with KH₂PO₄ or Na₂HPO₄ (pK_{ai} 2.15, 7.2 and 12.15):



So the apparent rate constant of a such reaction is probably strongly pH dependent. The published results showed that for pH < 1 the apparent rate constant of the oxidation of HCOOH with KMnO₄ or with Bi(V) varies linearly with 1/[H⁺] [3, 13]. The kinetic oxidation of HCOOH by BBCP also showed that the rate constant varies as [15].

In aqueous HClO₄, the apparent rate constants corresponding to the noncatalytic (nc) and autocatalytic (ac) reaction pathways are proportional to:

$$\left(\frac{K_1}{[H^+]} + K_1^{nc} + K_2^{ac} [H^+]^3 \right) [HCOOH] \quad (9)$$

In the present paper the kinetic study was done over a wide range of pH (0.3 < pH < 8). For pH lower than 1 the reaction is very slow. For pH > 7, the absorbance is not exploited due to the presence of undis-

solved MnO₂. For 1.5 < pH < 7 the results show unexpected behavior. The variation of the apparent rate constant versus pH does not follow a typical acid, base, or acid - base catalysis behavior [24]. The curve log k_{app} versus pH shows a maximum located between 4 and 5. Repetitive studies gave the same results. The position of the maximum varies little with [HCOOH] and with the presence of strong electrolyte used to fix the ionic strength (Fig. 5). It seems that the oxidation of formate is faster than with formic acid, but the formate concentration is not the only factor affecting the rate, since the rate constant versus pH does not show a plateau for pH higher than the pKa. It is possible that the apparent rate constant is a complex function of several other constants which are functions of several parameters. The pH corresponding to the highest rate constant corresponds to a compromise of all of these parameters.

The activation parameters associated with the oxidation of HCOOH are calculated according to the following: Plot of ln k_{app} vs. 1/T gives the value of activation energy E_a (Fig. 7) according to Arrhenius equation:

$$\ln K_{app} = -E_a / RT + \ln A \quad \text{with } R: 8.3J.K^{-1}.mol^{-1} \quad (5)$$

The activation enthalpy ΔH^\ddagger and the activation entropy ΔS^\ddagger can be calculated by applying Eyring equation:

$$\ln k_{app} = \ln \frac{K_B \times T}{h} + \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{R \times T} \quad (6)$$

where k_B = Boltzmann's constant (1.381x10⁻²³ J K⁻¹)
 h = Planck's constant (6.626x10⁻³⁴ J s).

The equation (6) can be rearranged in such a way that the plot of ln(k_{app}/T) vs. 1/T allows to determine ΔS^\ddagger and ΔH^\ddagger from the intercept and the slope, respectively.

The free activation enthalpy ΔG^\ddagger is equal to:

$$\Delta G^\ddagger = \Delta H^\ddagger - T \times \Delta S^\ddagger \quad (8)$$

The activation energy and the average of the other kinetics parameters in the temperature range studied (14-35°C) are listed below (Table 1). It seems that the oxidation occurs via several steps and the transient species is the same at any pH.

CONCLUSIONS

The kinetic study of the chemical oxidation of HCOOH with KMnO_4 over a wide range of pH (2-7) shows a great effect of pH and an unexpected variation of the rate constant with pH. The apparent rate constant passes through a maximum at pH between 4 and 5, which corresponds to a compromise of all parameters affecting the kinetics. The orders of the reaction are 1 and ~ 0.5 with respect to KMnO_4 and HCOOH. Davies equation plot predicts that the reaction occurs rather with the anion HCOO^- than with HCOOH even in acidic medium. ΔG^\ddagger was found to be independent of pH.

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