

Controlling the Kinetics of the Formic Acid Oxidation by Potassium Bromide

Yingchun Liu^{*,#}, Tao Yang[#]

Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China

[#]These authors contributed equally to this work.

*Corresponding author: liuyingch@zju.edu.cn

Abstract This study provides a strategy for controlling the kinetics of formic acid oxidation by potassium bromide. This strategy resolves the nonlinear deviation of the plot of electromotive force against time and ensures that formic acid oxidation follows first-order kinetics over a wide range of reaction temperatures. The methodology reported here should help instructors optimize their teaching efficiency and provides students with valuable insight into the control of chemical kinetics.

Keywords: controlling, kinetics of the formic acid oxidation, potassium bromide

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1. Introduction

Br₂ oxidizes formic (methanoic) acid to CO₂ in accordance with the following stoichiometric equation: HCOOH + Br₂ → CO₂ + 2H⁺ + 2Br⁻ (1). The progress of this reaction is described on the basis of HCOOH, Br₂, and H⁺ concentrations. Its progress can also be monitored electrochemically if it occurs in an electrochemical cell. The voltage or electromotive force (*EMF*) of the cell depends on the concentrations of Br₂ and Br⁻. Electrochemical monitoring is a highly convenient approach for following the reaction because the *EMF* is given by the voltmeter of the electrochemical cell as a function of time. The electrochemical cell has two electrodes. One electrode is simply a piece of Pt that is immersed in the solution. The reduction of Br₂ to Br⁻ occurs at this electrode, as follows: Br₂ + 2e⁻ → 2Br⁻ (2). The second electrode is a calomel (Hg₂Cl₂) electrode that consists of Hg metal in contact with a paste made of insoluble Hg₂Cl₂. The calomel electrode is surrounded by a saturated solution of KCl. The reaction that occurs at this electrode is Hg₂Cl₂ (s) + 2e⁻ → 2 Hg(m) + 2Cl⁻ (3). The saturated KCl solution is held in a glass container the surrounds Hg and Hg₂Cl₂. A small porous plug allows electrical contact between the KCl solution and any solutions that the Hg₂Cl₂ electrode is dipped into while preventing the two solutions from mixing. The *EMF* of a cell that comprises the Hg₂Cl₂ and Pt electrodes, which are immersed in a solution that contains Br⁻ and Br₂, depends on the concentrations of all the species involved in the two electrode reactions, as depicted in Eqns. (2) and (3). We add Br⁻ ions in such a large excess such that their concentrations remain unchanged during the experiment. Thus, any change in the *EMF* of the cell is attributable solely to the changes in Br₂ concentration ([Br₂]). The

relationship between the cell *EMF*, *E*, and [Br₂] can be explained as $E = \text{constant} + \ln [\text{Br}_2]$ (4). We are simply using the *EMF* as an indicator of [Br₂].

To ensure that [Br⁻] remains unchanged during the experiment, excess amounts of Br⁻ ions are added to the reaction system (20-fold of the amount of HCOOH and H⁺). However, in teaching practice, the reaction does not always follow first-order kinetics over a certain temperature range depending on the excess amount of Br⁻. Thus, the excess amount of Br⁻ is the key parameter that affects the kinetics of the reaction. The appropriate amount of Br⁻ ensuring that the reaction follows first-order kinetics should be determined and addressed during teaching. Coagulation rate can be reduced by decreasing the size of silica nanoparticles [1], and a kinetic study has been performed through absorption spectrophotometry [2]. However, the factors that affect the kinetics of HCOOH oxidation by KBr remain poorly understood. The present work investigates the factors that control the kinetics of HCOOH oxidation by KBr in detail. The appropriate amount of KBr required to ensure that the reaction follows first-order kinetics in teaching practice was studied extensively.

2. Methods

The rate law is assumed to be $\text{rate} = k [\text{HCOOH}]^a [\text{Br}_2]^b [\text{H}^+]^c$, where *a*, *b*, and *c* are orders with respect to HCOOH, Br₂, and H⁺, respectively. The experiment aims to determine these orders. An electrochemical cell facilitates the measurement of [Br₂]. Thus, the reaction rate can be conveniently expressed in terms of the rate of Br₂ loss, and the following equation is obtained through calculus: $d[\text{Br}_2] = -k [\text{HCOOH}]^a [\text{Br}_2]^b [\text{H}^+]^c dt$ (5). The negative sign in Eqn. (5) implies that [Br₂] decreases as the reaction progresses. To simplify the kinetics of this reaction, we

formulated reaction mixtures in which the amounts of HCOOH and H^+ are large excesses compared with those of Br_2 to ensure that the reactant concentrations remain constant throughout the reaction. The rate law can then be written as $d[Br_2]/dt = -k_{app} [Br_2]^b$, where $k_{app} = k[HCOOH]^a [H^+]^c$ (6). Here, initial k_{app} is the apparent rate constant and not a true rate constant because its value depends on the initial concentrations of HCOOH and H^+ . We first test the hypothesis that the order, with respect to Br_2 , is 1, that is, $b = 1$. The rate law can be then integrated as follows: $d[Br_2]/dt = -k_{app} [Br_2]$, $1/[Br_2] d[Br_2] = -k_{app} dt$, $\ln [Br_2] = -k_{app}t + A$ (7), where A is the constant of integration. The form of Eqn. (7) suggests that the reaction is the first order in Br_2 ; a plot of $\ln [Br_2]$ against t should provide a straight line with slope $-k_{app}$. Eqn. [4] demonstrates that the cell *EMF* is directly proportional to $\ln[Br_2]$, $E = \text{constant} + \ln [Br_2]$ (4). This equation can be rearranged to yield $\ln [Br_2] = E - (\text{constant})$. Substituting this expression for $\ln[Br_2]$ into Eqn. (7) yields $E - (\text{constant}) = -k_{app} t + B$ (8). This equation can be simplified as $E, k_{app} t, B$, where B is a constant at a given temperature. Equation (8) implies that the plot of E against time will present a straight line of slope $-k_{app}$. If E is given in volts and t is given in seconds, the usual SI units for all the other quantities provide an apparent first-order rate constant, k_{app} , in s^{-1} . When plotted in this way, the data should be fitted with a straight line, thus confirming that the reaction follows the first order in Br_2 .

3. Experimental

3.1 Apparatus

The following apparatuses were used: SunyLAB200 nonpaper recorder, precision super constant-temperature baths, saturated Hg_2Cl_2 electrode, Pt electrode, magnetic stirrer, thermostat jacket reactor, split voltage junction box, pipettes (5, 10, 25, and 50 mL), bottle washer, and suction bulb.

3.2. Reagent

The following reagents were used: 2.00 and 4.00 M HCOOH, 2.00 M HCl, 1 M KBr, 0.02 M Br_2 (0.0075 M Br_2 reagent was prepared), 1 M KBr, and deionized water.

3.3. Preliminary Steps

The nonpaper recorder, constant-temperature baths, and voltage junction box are connected with a wire. The power switch is turned on. The import and export of the thermostat jacket reactor are connected to the import and export of the constant-temperature bath trough, and the reactor is placed on the magnetic stirrer. The temperature of the constant-temperature baths is set to 25 °C. The reagents (75 mL of deionized water, 10 mL of KBr, 5 mL of HCl, and 5 mL of Br_2) are added to the reactor with a pipette. The total volume of reagents is 100 mL. The thermometer, Pt electrode, and Hg_2Cl_2 electrode are separately inserted into the reactor. Then, the magnetic stirrer is turned on, and the potentiometer of the voltage junction box is adjusted. The *EMF* is read on the nonpaper

recorder and allowed to reach a constant value after 5–10 minutes of continued magnetic stirring. The stabilization of *EMF* suggests that Br_2 has been completely produced. The stoichiometry of this reaction is expressed as follows: $5Br^- + BrO_3 + 6H^+ \rightarrow 3Br_2 + 3H_2O$. The *EMF* readings linearly increase with time after the addition of 5 mL of 0.1 M HCOOH. The reaction is stopped after 15–25 minutes. The *EMF* is plotted against time (in seconds). The best-fit straight line is then drawn and its slope is determined.

Separate kinetic runs at 25 °C, 30 °C, 35 °C, 40 °C, and 45 °C are conducted by changing the concentration of HCOOH (0.10 or 0.20 M) and the volumes of KBr (10, 15, 20, 25, 30, or 35 mL). The suggested sets of initial reactant solution concentrations, KBr volumes, and temperature are listed in Table 1.

Table 1. Suggested initial conditions of kinetic runs

Solution	Concentration (M)	Solution Pipette (mL)
HCOOH	0.10 M, 0.20 M	5
KBr	1.00 M	10, 15, 20, 25, 30, 35
HCl	2.00 M	5
Br_2 reagent	0.02 M	5
Water	Deionized water	75

4. Results and Discussion

4.1. Effect of the Amounts of KBr on the Kinetics of HCOOH Oxidation

The stoichiometry equation of this reaction shows that its rate decreases with the addition of different volumes of KBr. Table 2 indicates that the rate constant k decreases as the volume of KBr increases, and the rate constant k is larger under 0.2 M HCOOH than that under 0.1 M HCOOH. The change in *EMF* against time with the addition of different volumes of KBr at 25 °C is shown in Figure 1. The slopes of the best-fit straight lines for *EMF* against time sharply decrease when 10, 15, and 20 mL of KBr are added. This decrease, however, becomes gradual when 25, 30, and 35 mL of KBr are added. Thus, the decrease in the rate of HCOOH oxidation depends on the added volumes of KBr. Time and *EMF* are linearly related. This relationship indicates that the reaction follows first-order kinetics. Therefore, the addition of different volumes of KBr affects the kinetics of HCOOH oxidation.

Table 2 Rate of HCOOH oxidation at 25 °C with the addition of different volumes of KBr

KBr/mL	HCOOH/mol·L ⁻¹	slope	rate/mol·L ⁻¹ ·S ⁻¹	R
10	0.1	0.0538	4.1883	0.99991
15	0.1	0.0304	2.3617	0.99992
20	0.1	0.0259	2.0165	0.99993
25	0.1	0.0216	1.6847	0.99993
30	0.1	0.0199	1.5531	0.99993
35	0.1	0.0174	1.3355	0.99993
10	0.2	0.0881	6.9787	0.99990
15	0.2	0.0708	5.6088	0.99991
20	0.2	0.0564	4.4639	0.99992
25	0.2	0.0479	3.7919	0.99993
30	0.2	0.0281	2.2269	0.99993
35	0.2	0.0271	2.1458	0.99993

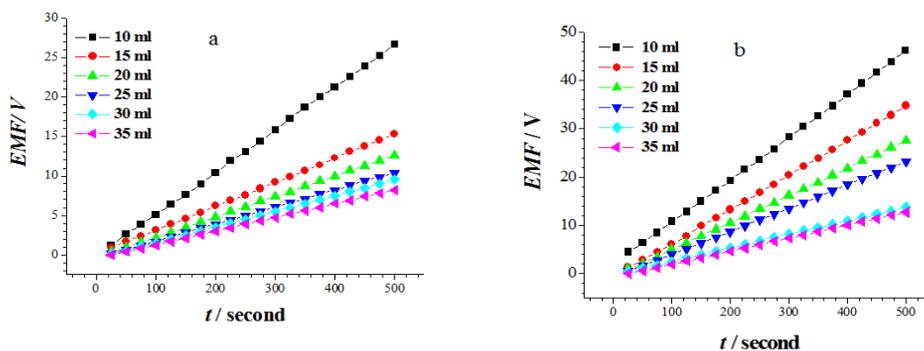


Figure 1. Plots of *EMF* against time for the (a) 0.1 and (b) 0.2 M HCOOH reaction systems with different volumes of KBr at 25 °C

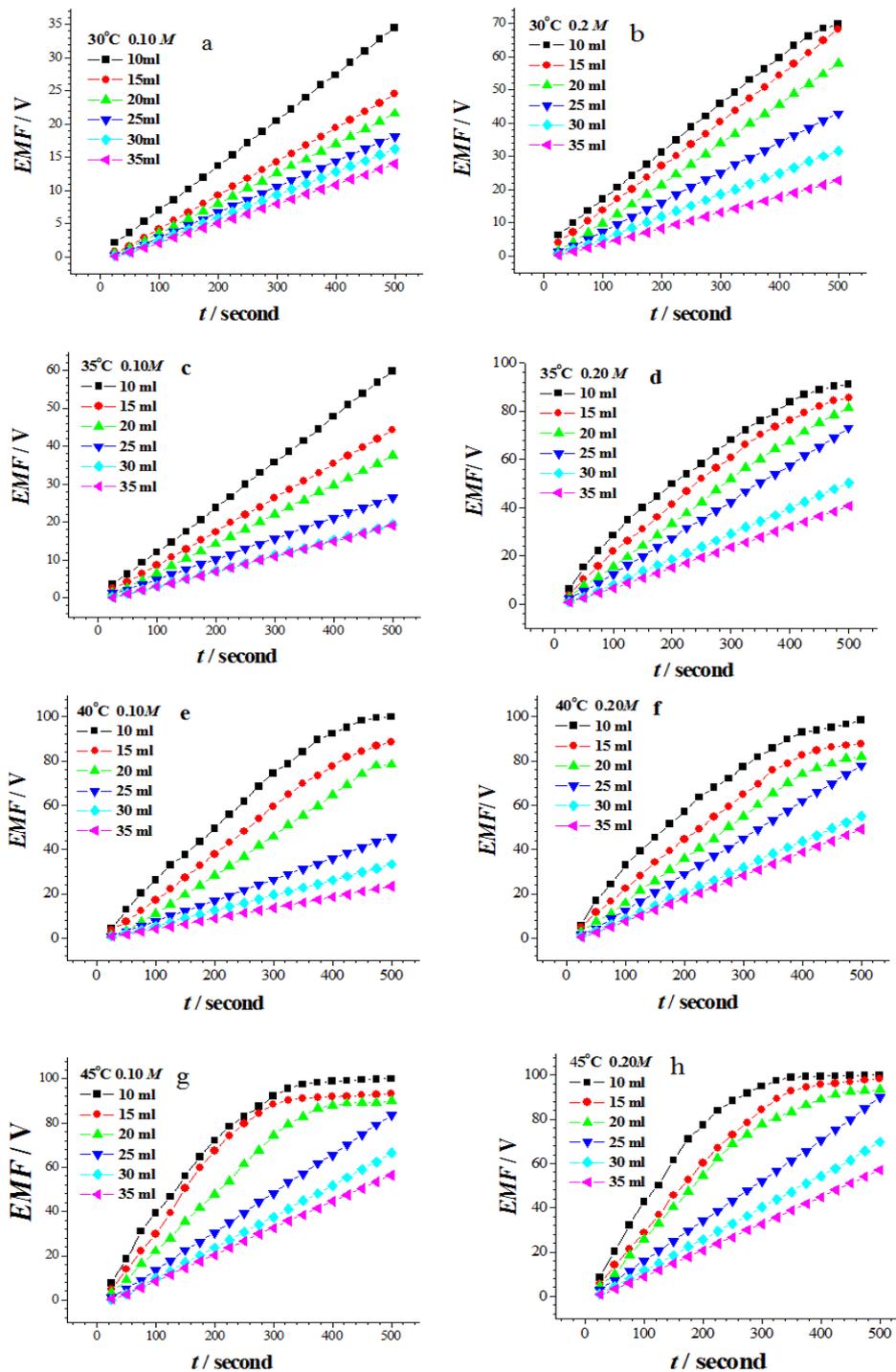


Figure 2. Plots of *EMF* against time for the 0.10 M(a, c, e, g) and 0.20 M HCOOH (b, d, f, h) reaction systems with different volumes of KBr over 30 °C, 35 °C, 40 °C, and 45 °C

4.2. Effect of Temperature on the Kinetics of HCOOH Oxidation

In practice, under initial conditions and increasing temperature, the relationship between *EMF* and time is nonlinear. Thus, the effect of temperature on reaction kinetics should be explored. Figure 2 shows the change in *EMF* against time under different volumes of KBr over the temperature range of 30 °C–45 °C for the 0.10 M HCOOH (a, c, e, g) and 0.20 M HCOOH (b, d, f, h) systems. The slopes of the 0.10 and 0.20 M HCOOH reaction systems increases as the temperature increases, and the reaction order is temperature-sensitive. The curve of *EMF* against time is correlated with the reaction kinetics. If the curve of *EMF* against time is linear, then the reaction follows first-order kinetics. Otherwise, the reaction follows second-order kinetics if the relationship between *EMF* and time is nonlinear. For the 0.10 M HCOOH system, the relationship between *EMF* and time is linear if the temperature is lower than 30 °C for all volumes of KBr, indicating that the reaction follows first-order kinetics.

The plot is nonlinear and the reaction order changes if the volume of KBr is less than 25 mL. Therefore, the kinetics of HCOOH oxidation can be controlled through the addition of different volumes of KBr. Thus, the oxidation kinetics of the 0.10 M HCOOH reaction system over the temperature range of 25 °C–45 °C can be controlled through the addition of 25–35 mL of KBr.

To investigate the effect of temperature, the plots of

EMF against time for the 0.1 and 0.2 M HCOOH systems with The reaction order and relationship followed by the 0.20 M HCOOH reaction system is almost the same as those followed by the 0.10 M HCOOH reaction system. However, the 0.20 M HCOOH reaction system is more sensitive to temperature than the 0.10 M HCOOH reaction system. Specifically, when the temperature exceeds 35 °C and the volume of KBr is less than 25 mL, the relationship between *EMF* and time is nonlinear (Figure 2 d, f, h). The nonlinear deviation of the curve becomes more pronounced with increasing temperature. Conversely, the plot of *EMF* against time is linear if the volumes of KBr exceed 25 mL under all temperatures, and the reaction order follows first-order kinetics. The same volumes of KBr at different temperatures were compared. As shown in Figure 3, when the volumes of KBr are 10, 15, and 20 mL, the plots of the 0.1 and 0.2 M HCOOH reaction systems appear linear over the temperatures of 25 °C and 30 °C. This result indicates that the reaction follows first-order kinetics. Otherwise, the reaction follows second-order kinetics under increasing temperatures as indicated by the fitting of the correlation coefficient by a third-order square. In general, the slope of the plot of the 0.2 M HCOOH reaction system is larger than that of the plot of the 0.1 M HCOOH reaction system, indicating that the reaction rate of the former system is faster than that of the latter. Meanwhile, as shown in Figure 4, if the volumes of KBr exceed 25 mL, all the plots are linear at 25 °C – 45 °C. Thus, the reaction kinetics can be controlled by adjusting the volume of KBr.

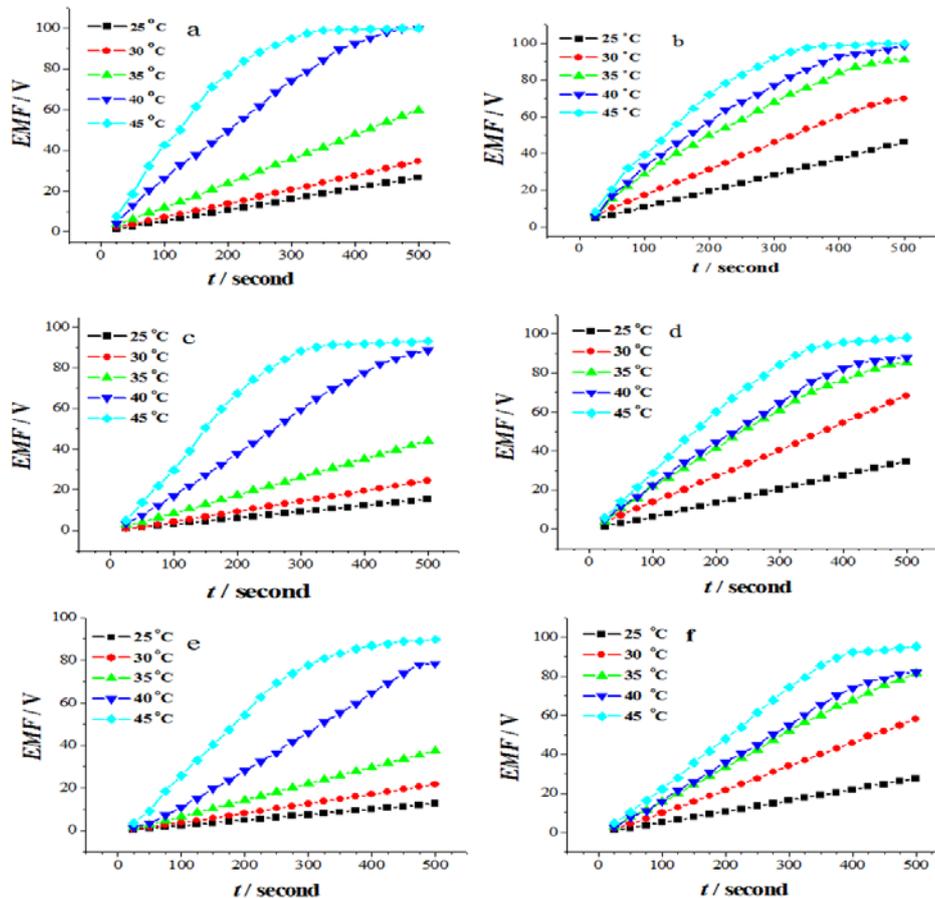


Figure 3. Plots of *EMF* against time for the 0.10 (a, c, e) and 0.20 M HCOOH (b, d, f) reaction systems under different temperatures with the addition of 10 (a, b), 15 (c, d), or 20 mL (e, f) of KBr

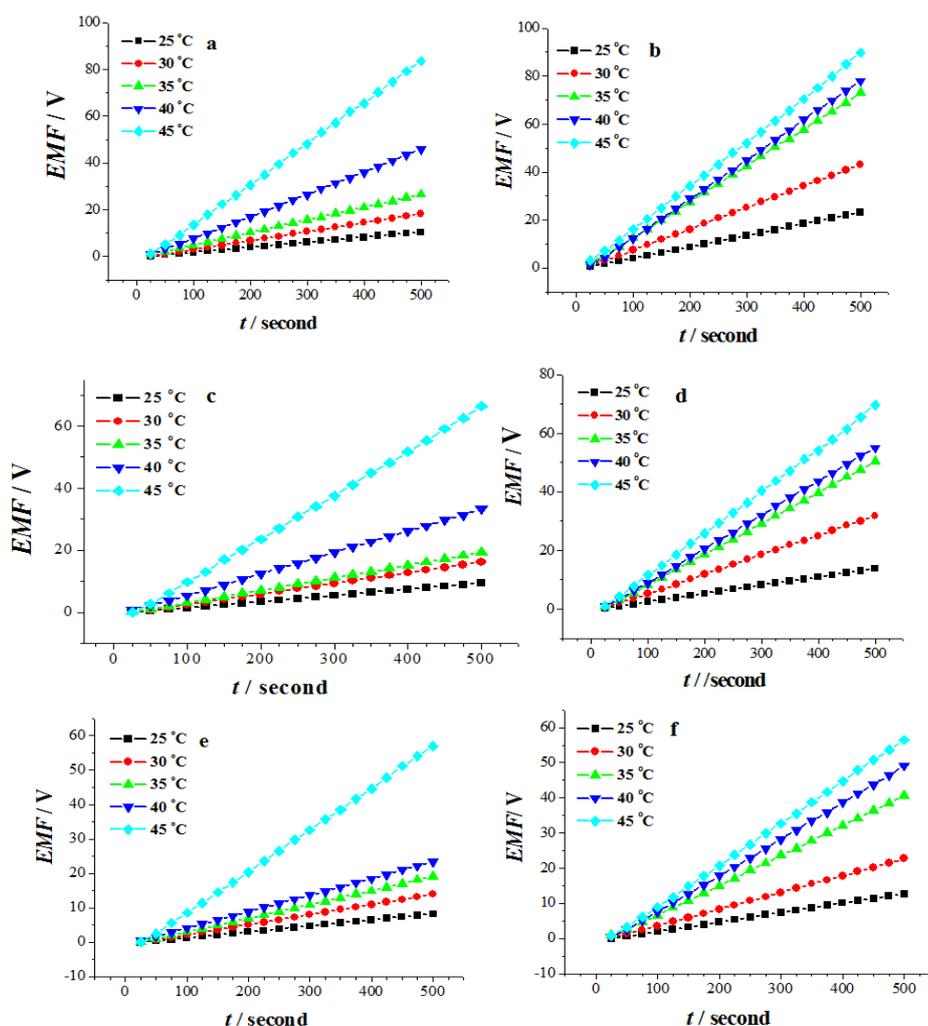


Figure 4. Plots of EMF against time for the 0.10 (a, c, e) and 0.20 M HCOOH (b, d, f) reaction systems under different temperatures with the addition of 25 (a, b), 30 (c, d), or 35 mL (e, f) of KBr

5. Conclusion

The reaction rates of HCOOH oxidation are adjusted through the addition of different volumes of KBr. HCOOH oxidation under the reaction temperatures of less than 35 °C can be controlled to follow first-order kinetics through the addition of 10-35 mL of KBr. This effect is confirmed by the linear relationship between EMF and time at 35 °C. However, if the reaction temperature exceeds 35 °C, the reaction rate increases, the curves of EMF against time become nonlinear, and the reaction follows second-order kinetics. Furthermore, if the added volumes of KBr exceed 25 mL, the reaction rate decelerates and the curve of EMF against time becomes linear over the temperature range of 25 °C-35 °C, indicating that temperature and concentration do not affect the reaction order under the present conditions. Therefore, the addition of KBr is an effective approach to control the kinetics of HCOOH oxidation. This approach can be widely applied in laboratory work.

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