Preparation of peracetic acid from hydrogen peroxide
Part I: Kinetics for peracetic acid synthesis and hydrolysis

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Abstract

A homogeneous kinetic model for preparation of peracetic acid (PAA) from acetic acid (AA) and hydrogen peroxide (HP) under the catalysis of sulfuric acid (SA) in the liquid phase was investigated. The kinetic equations of PAA synthesis and hydrolysis were given and the kinetic constants were estimated according to the experimental data by a simplex optimization method. It was found that the synthesis and hydrolysis of PAA were both first-order reactions with respect to reactant concentrations and H^+ concentration. Linear relationships were discovered between the observed rate constants and H^+ concentrations at a certain temperature, with the slopes being corresponding intrinsic rate constants. The intrinsic activation energies of PAA synthesis and hydrolysis were 57.8 and 60.4 kJ mol^{-1}, respectively. The mechanisms of PAA synthesis and hydrolysis were discussed. It has been proved that the rate-determining step in the synthesis of PAA is the reaction between H_2O_2 with active carbonyl intermediary, and in the hydrolysis of PAA the reaction between water and corresponding active carbonyl intermediary.
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Keywords: Peracetic acid; Hydrogen peroxide; Kinetics; Synthesis; Hydrolysis; Reaction mechanism

1. Introduction

Peracetic acid (PAA) is a strong oxidant with reduction potential of 1.06 V, which is similar to that of traditional bleaching agent, chlorine dioxide [1]. It has been applied in disinfection [2,3], bleaching of textiles and pulps [4–7], epoxidation of olefins [8,9], and so on. Recently, environmental concerns and market pressure are forcing the pulp and paper industry to explore alternatives to conventional chlorine containing chemicals. Some researches have shown that PAA is a less capital intensive, easily retrofit and highly selective totally chlorine-free (TCF) bleaching agent when used under the optimum conditions [10].

Generally, PAA can be prepared in two ways, namely from hydrogen peroxide (HP) or by oxidation of acetaldehyde, and the latter can be operated in a liquid phase or vapour phase [11]. For many years the most commonly used method for preparing PAA has been the former way, either with acetic acid (AA)

(see Eq. (1)) or with acetic anhydride (AAh) (see Eq. (2)). The AAh–HP reaction is exothermic and difficult to control, and the possible formation of diacetyl peroxide leads to increased explosion hazards [11]. Therefore, the AA–HP reaction is preferred in common preparation of PAA. This reaction is reversible and thus an equilibrium mixture of reactants and products is obtained. The rate at which equilibrium is achieved can be accelerated by adding a strong acid catalyst, usually sulfuric acid (SA):

$$CH_3COOH + H_2O_2 \underset{}{\overset{H_2SO_4}{\rightleftharpoons}} CH_3COOOH + H_2O \qquad (1)$$

$$(CH_3CO)_2O + 2H_2O_2 = 2CH_3COOOH + H_2O \qquad (2)$$

Many studies have shown that the concentration of equilibrium PAA varied with the HP concentration and molar ratio of AA:HP. The charge of sulfuric acid used also differed from 0 to 9% [11–13]. Some studies reported the decomposition or hydrolysis of peracetic acid in aqueous solutions [14–17]. All of these researches have shown that the hydrolysis of PAA were first-order with respect to PAA concentration. Only a few studies referred to the equilibrium kinetics of PAA preparation by the reaction of AA and HP [13,18]. However, in these researches no mathematical expressions for calculation of kinetic constants

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Nomenclature

a	activity
A_1	pre-exponential factor of peracetic acid synthesis ($L\,mol^{-2}\,h^{-2}$)
A_2	pre-exponential factor of peracetic acid hydrolysis ($L\,mol^{-2}\,h^{-2}$)
b_B	concentration of ion B ($mol\,kg^{-1}$)
C_X	concentration of species X ($mol\,L^{-1}$)
C_{X0}	initial concentration of species X ($mol\,L^{-1}$)
E_{a1}	intrinsic activation energy of peracetic acid synthesis ($kJ\,mol^{-1}$)
E_{a2}	intrinsic activation energy of peracetic acid hydrolysis ($kJ\,mol^{-1}$)
I	ionic strength
k_1	intrinsic rate constant of peracetic acid synthesis ($L\,mol^{-2}\,h^{-2}$)
k_{1obs}	observed rate constant of peracetic acid synthesis ($L\,mol^{-1}\,h^{-1}$)
k_2	intrinsic rate constant of peracetic acid hydrolysis ($L\,mol^{-2}\,h^{-2}$)
k_{2obs}	observed rate constant of peracetic acid hydrolysis ($L\,mol^{-1}\,h^{-1}$)
$K_{a,AcH}$	thermodynamic dissociation constant of acetic acid
$K_{C,AcH}$	concentration dissociation constant of acetic acid
T	reaction temperature (K)
z_B	charge number of ion B

Greek letters

α	degree of dissociation of acetic acid
γ	activity coefficient

were given. The objective of this paper is to develop a kinetic model for PAA synthesis and hydrolysis in the presence of sulfuric acid in the liquid phase, the effects of ionic strength and H$^+$ concentration being considered. The kinetic constants of forward and reverse reactions were obtained by fitting the experimental data, and corresponding mathematical expressions for kinetic constants were given.

2. Experimental

All the chemicals were analytically pure and purchased locally. Before the reaction, certain volumes of AA and SA were put in 100 ml clean ground-glass stoppered flasks. Then certain volumes of 30% HP were added and mixed homogeneously. The initial volume ratio of AA and 30% HP was 1.5. The system was kept at a constant temperature in a water bath. Samples were taken and quickly analyzed in accordance with the Chinese Standard GB/T 19108-2003, which was the iodometric method. Each datum was the average result of at least double tests. Deioned water was used in all the experiments. The kinetic constants were obtained by fitting experimental data by a simplex optimization method using MATLAB 6.5 software.

3. Results and discussion

3.1. Postulations of kinetic model

Before developing the kinetic model, some proper postulations should be made to make the system easier. These postulations are as follows:

(1) The volume of liquid reaction system keeps constant during reaction at a certain temperature.
(2) The pK_a value of AA at 298 K is 4.76 and does not change in the temperature span of 293–323 K, and so is the pK_a value of PAA.
(3) The pK_a value of PAA at 298 K is 8.2 [10], which is much larger than that of AA. Thus, the dissociation of PAA in acid condition can be negligible.
(4) The thermal decomposition of HP and spontaneous decomposition of PAA in this temperature span can be also negligible. Actually, HP is very stable when no catalyst exists, even at a higher temperature. And thermal homolysis of PAA becomes obvious only at a higher temperature than 80 °C [17]. Besides, there is much water existing in the system, and it is a stronger nucleophilic group than H$_2$O$_2$ and CH$_3$COOH. Therefore, the consumption of PAA is mainly due to its hydrolysis.

So the reactions in this system mainly consist of two reactions, synthesis and hydrolysis of PAA:

$$CH_3COOH(A) + H_2O_2(B) \underset{k_2}{\overset{H_2SO_4, k_1}{\rightleftharpoons}} CH_3COOOH(C) + H_2O(D) \tag{3}$$
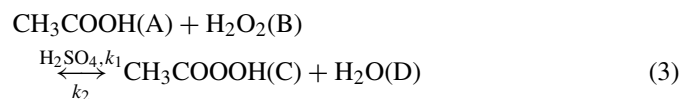
3.2. Development of kinetic model

According to Eq. (3), a homogenous kinetic model can be developed as follows:

$$\frac{dC_B}{dt} = k_{2obs}C_CC_D - k_{1obs}C_AC_B \tag{4}$$

$$\frac{dC_C}{dt} = k_{1obs}C_AC_B - k_{2obs}C_CC_D \tag{5}$$

where k_{1obs} and k_{2obs} are observed rate constants for forward and reverse reactions, respectively. As these reversible reactions are acid-catalyzed reactions, the observed rate constants must be the function of H$^+$ concentration ([H$^+$]). So, we can assume that k_{1obs} and k_{2obs} could be written as the following formulas: $k_{1obs} = k_1[H^+]^\alpha$, $k_{2obs} = k_2[H^+]^\beta$, where k_1 and k_2 are intrinsic rate constants for the forward and reverse reactions. α and β are corresponding reaction orders. According to mass conservation, the concentrations of AA and water can be calculated with their initial concentrations and PAA concentration: $C_A = C_{A0} - C_C$, $C_D = C_{D0} + C_C$. Thus, the kinetic equations can be written as:

$$\frac{dC_B}{dt} = k_{2obs}C_C(C_{D0} + C_C) - k_{1obs}(C_{A0} - C_C)C_B \tag{6}$$

$$\frac{dC_C}{dt} = k_{1obs}(C_{A0} - C_C)C_B - k_{2obs}C_C(C_{D0} + C_C) \tag{7}$$

In the system, H^+ mainly comes from two parts, dissociation of sulfuric acid and AA, namely:

$$[H^+] = [H^+]_{AcH} + [H^+]_{H_2SO_4} \tag{8}$$

The dissociation of AA is controlled by the equilibrium:

$$CH_3COOH \leftrightarrow CH_3COO^- + H^+ \tag{9}$$

with

$$
K_{a,AcH} = \frac{a_{CH_3COO^-} a_{H^+}}{a_{CH_3COOH}}
$$
$$
= \frac{\gamma_{CH_3COO^-} \gamma_{H^+}}{\gamma_{CH_3COOH}} K_{C,AcH} = 1.75 \times 10^{-5} \tag{10}
$$

where $K_{a,AcH}$ and $K_{C,AcH}$ are thermodynamic dissociation constant and concentration dissociation constant of AA, respectively. a and γ are activity and activity coefficient, respectively, with their relation of $a = \gamma C$. The activity coefficient γ can be calculated by Davies' formula:

$$\ln \gamma = -1.171|z_+ z_-| \left[\frac{\sqrt{\{I\}}}{1 + \sqrt{\{I\}}} - 0.30\{I\} \right] \tag{11}$$

where $\{I\}$ denotes the value of ionic strength I. In our models, I was calculated approximatively from molar concentration of species:

$$
I = \frac{1}{2}(b_{H^+} + b_{CH_3COO^-} + 4b_{SO_4^{2-}}) = \frac{1}{2}(2b_{CH_3COO^-} + 6b_{SO_4^{2-}})
$$
$$
= b_{CH_3COO^-} + 3b_{SO_4^{2-}} \approx C_A \alpha + 3C_{SO_4^{2-}} \tag{12}
$$

where α is the degree of dissociation of AA. So the H^+ concentration can be obtained by the following expressions:

$$[H^+] = \frac{2C_{SO_4^{2-}} + \sqrt{(2C_{SO_4^{2-}})^2 + 4(C_{A0} - C_C)K_{C,AcH}}}{2} \tag{13}$$

It is clear that when the charge of sulfuric acid is too small, H^+ from AA is not negligible. But when the charge of sulfuric acid is large enough, the H^+ in the system can be thought being only from complete dissociation of sulfuric acid.

3.3. Determination of kinetic constants

The comparison of calculated data and experimental data of PAA and HP concentrations versus time at several reaction temperatures are shown in Figs. 1 and 2. It is clear that the model well predicts the concentrations of PAA and HP during the reaction. The values of k_{1obs} and k_{2obs} determined by fitting experimental data with our kinetic models are shown in Tables 1 and 2, respectively. We can see that with the increase in reaction temperature

Table 1
Values of k_{1obs} (L mol^{-1} h^{-1}) at different temperatures with different H^+ concentration

H^+ concentration (mol L^{-1})	T (K)			
	293	303	313	323
0.0018	0.000461	0.001040	0.001993	0.004113
0.0250	0.001356	0.002563	0.004991	0.008944
0.1250	0.003381	0.008575	0.018244	0.046263
0.2500	0.007725	0.016113	0.034500	0.079450
0.6250	0.021313	0.048969	0.083156	0.200563

Table 2
Values of k_{2obs} (L mol^{-1} h^{-1}) at different temperatures with different H^+ concentration

H^+ concentration (mol L^{-1})	T (K)			
	293	303	313	323
0.0018	0.000076	0.000309	0.000980	0.001855
0.0250	0.000746	0.001265	0.002040	0.003806
0.1250	0.001206	0.003238	0.007763	0.018613
0.2500	0.002863	0.006000	0.013538	0.032225
0.6250	0.007281	0.017250	0.029770	0.075750

or H^+ concentration, k_{1obs} and k_{2obs} were both increased. It indicates the forward and reverse reactions are both acid-catalyzed processes, which is in accordance with the conclusions of some literatures [13,18].

The plots of k_{1obs} versus $[H^+]$ and k_{2obs} versus $[H^+]$ are shown in Fig. 3, and the linear fitting results are summarized in Table 3. It has indicated a good linear relationship between k_{1obs} and $[H^+]$ or k_{2obs} and $[H^+]$, which shows that the synthesis and hydrolysis of PAA are both first-order reactions with respect to H^+ concentration. Similar results were also obtained according to Koubek's studies [15]. Table 3 also summarizes the intrinsic rate constants for the forward and reverse reactions estimated from the slopes of linear plots. So we can get the conclusion that the synthesis of PAA by the reaction of AA and HP is first order

$$K_{C,AcH} \approx \frac{1.75 \times 10^{-5}}{\exp\{-2.342[\sqrt{(C_{A0} - C_C)\alpha + 3C_{SO_4^{2-}}}/(1 + \sqrt{(C_{A0} - C_C)\alpha + 3C_{SO_4^{2-}}}) - 0.30[(C_{A0} - C_C)\alpha + 3C_{SO_4^{2-}}]]\}} \tag{14}$$

with respect to AA concentration, HP concentration and as well as acid concentration. Similarly, the hydrolysis of PAA in acid

Table 3
Results of linear fitting of k_{1obs} vs. $[H^+]$ and k_{2obs} vs. $[H^+]$

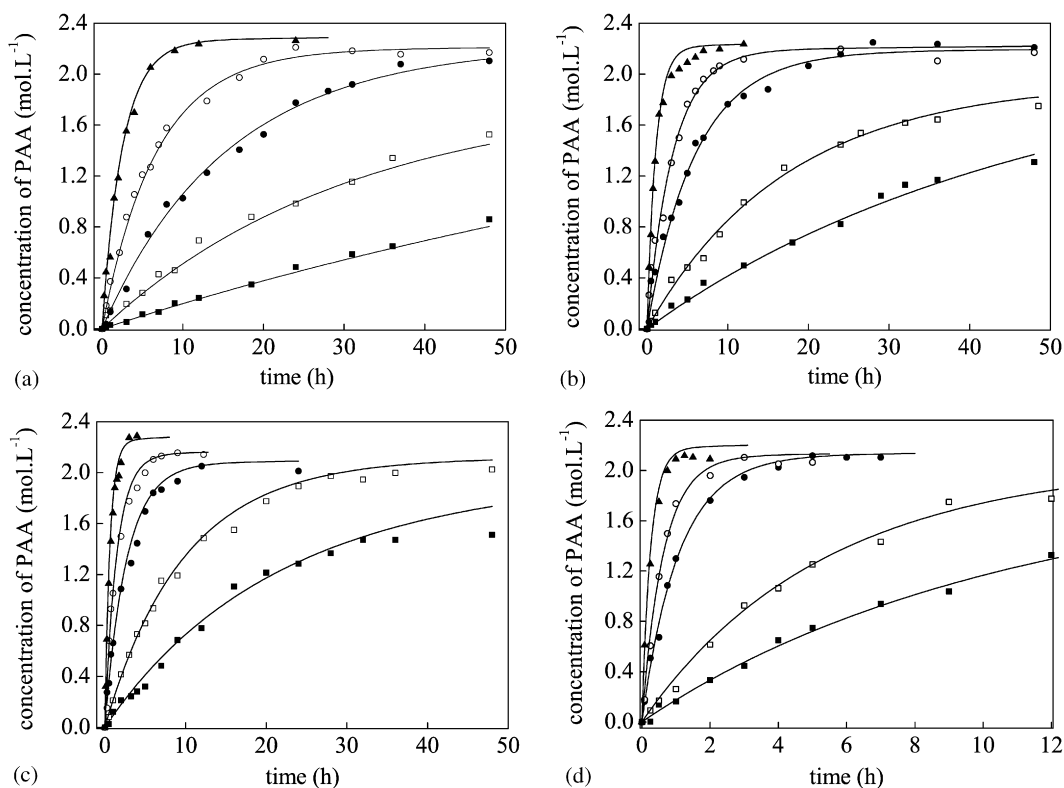| k_1 (L mol^{-2} h^{-2})	T (K)			
	293	303	313	323
	0.03347	0.07621	0.13423	0.32219
R	0.99720	0.99604	0.99999	0.99952
S.D.	0.00064	0.00177	0.00153	0.00357
k_2 (L mol^{-2} h^{-2})	0.01158	0.02710	0.04903	0.12320
R	0.99636	0.99704	0.99869	0.99930
S.D.	0.00026	0.00053	0.00128	0.00207

Fig. 1. Experimental and calculated concentrations of PAA at several temperatures with different charge of sulfuric acid as catalyst: (a) $T = 293$ K; (b) $T = 303$ K; (c) $T = 313$ K; (d) $T = 323$ K. (■) 0.00 mol L^{-1} H$_2$SO$_4$; (□) 0.0125 mol L^{-1} H$_2$SO$_4$; (●) 0.0626 mol L^{-1} H$_2$SO$_4$; (○) 0.125 mol L^{-1} H$_2$SO$_4$; (▲) 0.3125 mol L^{-1} H$_2$SO$_4$;—calculated values.
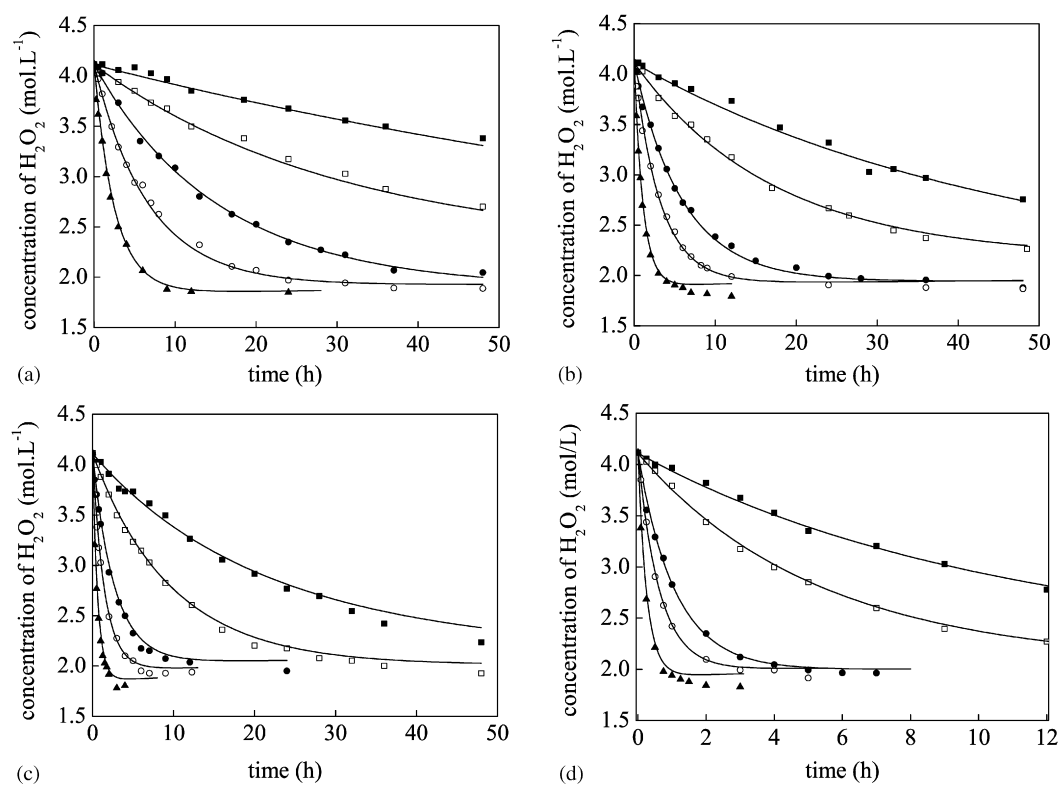
Fig. 2. Experimental and calculated concentrations of HP at several temperatures with different charge of sulfuric acid as catalyst: (a) $T = 293$ K; (b) $T = 303$ K; (c) $T = 313$ K; (d) $T = 323$ K. (■) 0.00 mol L^{-1} H$_2$SO$_4$; (□) 0.0125 mol L^{-1} H$_2$SO$_4$; (●) 0.0626 mol L^{-1} H$_2$SO$_4$; (○) 0.125 mol L^{-1} H$_2$SO$_4$; (▲) 0.3125 mol L^{-1} H$_2$SO$_4$;—calculated values.
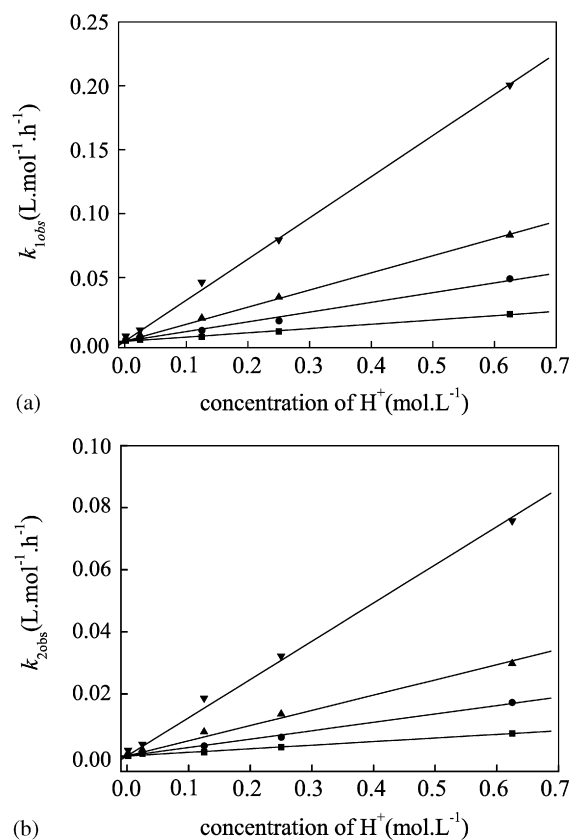
Fig. 3. Linear plots of k_{1obs} vs. [H$^+$] and k_{2obs} vs. [H$^+$]: (a) k_{1obs} vs. [H$^+$]; (b) k_{2obs} vs. [H$^+$]. (■) 293 K; (●) 303 K; (▲) 313 K; (▼) 323 K.

environment is first order with respect to PAA concentration, water concentration and as well as acid concentration. Kunigk et al. found the decomposition of PAA was a first-order reaction at 25–45 °C when the initial PAA concentrations were 240 and 280 mg L^{-1}[16]. However, they did not mention the exact reaction mechanisms and the relationship between decomposition rate constants and H$^+$ concentration. According to our results, we think that in this temperature range the decomposition of PAA referred to in their studies must be the hydrolysis process of PAA.

The intrinsic activation energies of PAA synthesis and hydrolysis from the Arrhenius plots of data shown in Table 3 are 57.8 and 60.4 kJ mol^{-1}, respectively (see Fig. 4), comparable with the decomposition activation energy of 66.2 kJ mol^{-1} obtained in Kunigk's studies [16]. An important aspect which should be noted is that the forward and reverse reactions have similar values of activation energy. It indicates the temperature affects the two reactions in similar degrees. However, the values of activation energy in our study are much larger than Dul'neva's results (14.22 ± 3.49 kJ mol^{-1} for the forward reaction and 27.90 ± 3.39 kJ mol^{-1} for the reverse reaction) [13]. Their data were obtained in the presence of 0.057 M H$_2$SO$_4$ in the system, so the activation energies must be observed activation energies, rather than intrinsic activation energies. This also proves that both of the forward and reverse reactions are acid-catalyzed processes.
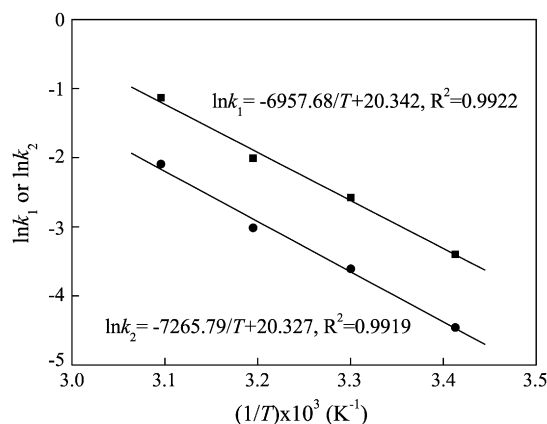

Fig. 4. The Arrhenius plots of the intrinsic rate constants and temperatures (■) for k_1; (●) for k_2.

Therefore, the intrinsic reaction rate constants, k_1 and k_2, at different temperatures (in Kelvin) can be calculated from the following expressions:

$$k_1 = 6.83 \times 10^8 \exp\left(-\frac{57846.15}{RT}\right) \quad (15)$$

$$k_2 = 6.73 \times 10^8 \exp\left(-\frac{60407.78}{RT}\right) \quad (16)$$

Corresponding observed rate constants, k_{1obs} and k_{2obs}, follow the expressions as:

$$k_{1obs} = [H^+] \times 6.83 \times 10^8 \exp\left(-\frac{57846.15}{RT}\right) \quad (17)$$

$$k_{2obs} = [H^+] \times 6.73 \times 10^8 \exp\left(-\frac{60407.78}{RT}\right) \quad (18)$$

3.4. Reaction mechanisms

The mechanisms of PAA synthesis and hydrolysis have been proposed [13,18,19]. Using an ^{18}O isotope label, it was found that the reaction did not involve dissociation of the O—O bond in initial hydrogen peroxide [20]. The hydrolysis of peroxyacids synthesized from HC^{18}OOH or CH$_3$C^{18}OOH and H$_2$O$_2$ afforded hydrogen peroxide containing no heavy oxygen (^{18}O). This means that in both of the formation and hydrolysis of peroxyacids, the bond between the acyl group and oxygen atom is cleaved [13]. Rubio et al. studied the mechanism of formation of peracids taking the reaction between formic acid and hydrogen peroxide as a model for generation of performic acid. He proposed two different routes for the formation of performic acid, Route A and Route B. Route A consists of the addition of the hydrogen peroxide to the carbonyl carbon for the formation of a tetrahedral transitional state with the subsequent loss of a water molecule, while Route B is carried out in an acid medium for the activation of the carbonyl carbon and the subsequent addition of the hydrogen peroxide and the loss of a water molecule [19]. It is obvious that Route B is preferred, even on the occasion that no acid catalyst exits in the reaction system, because the organic acid (acetic acid or formic acid) can dissociate H$^+$, which can
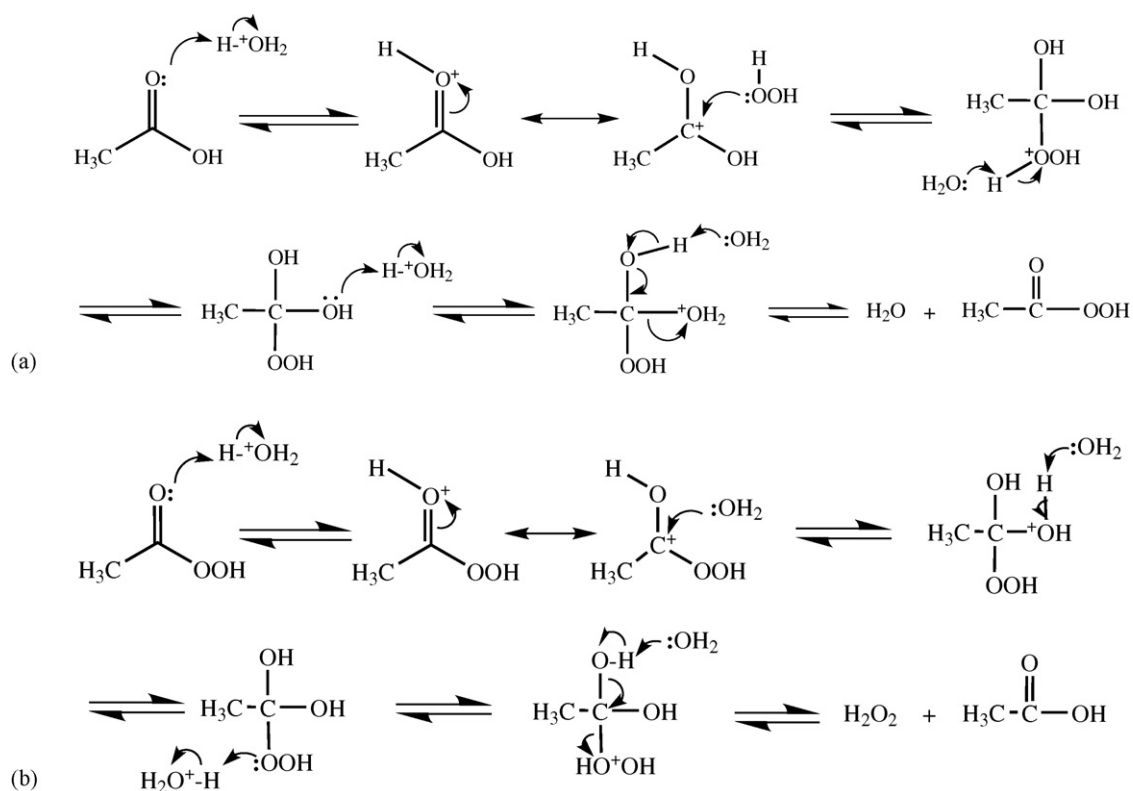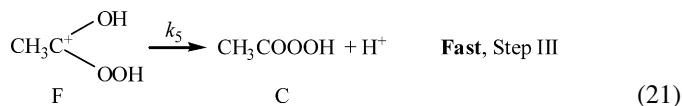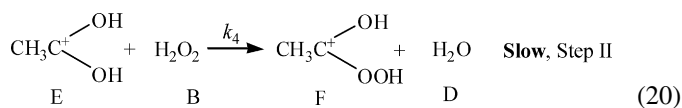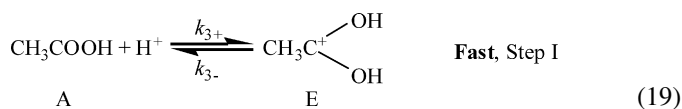
Fig. 5. Reaction mechanisms of PAA synthesis and hydrolysis with acid-catalysis: (a) PAA synthesis; (b) PAA hydrolysis.

further accelerate the reaction. So the forward and reverse processes may be described by the detailed schemes containing the moving of electrons, as shown in Fig. 5.

However, as to the rate-determining step, different researchers gave different conclusions. Kharchuk et al. claimed that in acid-catalytic decomposition of peracetic acid, the controlling step was the protonation of PAA followed by the reaction of the active intermediate form [14]. Dul'neva claimed that the rate-determining step in the forward reaction was elimination of water molecule from oxonium ion, and in the reverse reaction was the elimination of hydrogen peroxide [13]. Sawaki and Ogata claimed that the rate-determining step was the reaction between the actived carbonyl with hydrogen peroxide in the forward reaction or water in the reverse reaction [18]. However, Rubio et al. gave the conclusion that the determinant stage of the generation of peracids was the formation of the neutral tetrahedral intermediary [19]. In order to determine which step is the rate-determining step, we presume the synthesis of PAA follows the following three steps:

$$CH_3COOH + H^+ \underset{k_{3-}}{\overset{k_{3+}}{\rightleftharpoons}} CH_3C^{+}{\overset{OH}{<}}_{OH} \qquad \textbf{Fast, Step I}$$
$$\qquad A \qquad\qquad\qquad E \qquad\qquad\qquad\qquad (19)$$

$$CH_3C^{}{\overset{OH}{<}}_{OH} + H_2O_2 \overset{k_4}{\longrightarrow} CH_3C^{}{\overset{OH}{<}}_{OOH} + H_2O \quad \textbf{Slow, Step II}$$
$$\quad E \qquad\quad B \qquad\qquad F \qquad\qquad D \qquad\qquad (20)$$

$$CH_3C^{+}{\overset{OH}{<}}_{OOH} \overset{k_5}{\longrightarrow} CH_3COOOH + H^+ \qquad \textbf{Fast, Step III}$$
$$\quad F \qquad\qquad\qquad C \qquad\qquad\qquad\qquad (21)$$

The first step is the protonation of the carbonyl oxygen of acetic acid resulting in formation of an active intermediary E. A pre-equilibrium is employed for this step, which means the rate of formation of E and its decay back into reactants are much faster than its rate of formation of products, F and water. The step II is presumed to be the rate-determining step. The third step is also fast, namely $k_5 \gg k_4$, which implies the intermediary F can transform to peracetic acid very quickly. So we can obtain the rate of formation of PAA as:

$$\left.\frac{dC_C}{dt}\right|_{synthesis} \approx -\frac{dC_F}{dt} = k_4 C_E C_B \qquad (22)$$

Since we assume that A, H$^+$ and E are in equilibrium, we can write:
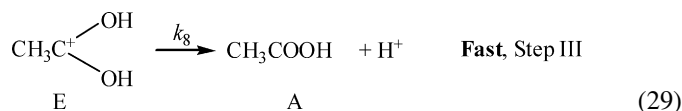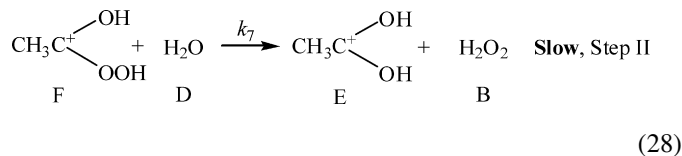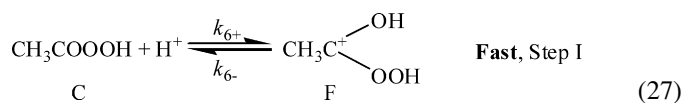
$$k_{3+}[H^+]C_A = k_{3-}C_E \qquad (23)$$

Thus, the concentration of E can be expressed as:

$$C_E = \frac{k_{3+}}{k_{3-}}[H^+]C_A \qquad (25)$$

The rate of synthesis of PAA now may be written as:

$$\left.\frac{dC_C}{dt}\right|_{synthesis} = \frac{k_4 k_{3+}}{k_{3-}}[H^+]C_A C_B = k_1[H^+]C_A C_B$$
$$= k_{1obs}C_A C_B \qquad (26)$$

Analogously, the hydrolysis of PAA can be presumed to following the similar schemes:

$$CH_3COOOH + H^+ \underset{k_{6-}}{\overset{k_{6+}}{\rightleftharpoons}} CH_3C\underset{OOH}{\overset{OH}{\diagdown}} \quad \textbf{Fast, Step I}$$

$$\qquad C \qquad\qquad\qquad\qquad F \qquad\qquad\qquad\qquad (27)$$

$$CH_3C\underset{OOH}{\overset{OH}{\diagdown}} + H_2O \xrightarrow{k_7} CH_3C\underset{OH}{\overset{OH}{\diagdown}} + H_2O_2 \quad \textbf{Slow, Step II}$$

$$\quad F \qquad\quad D \qquad\qquad\qquad E \qquad\qquad B$$

$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad (28)$$

$$CH_3C\underset{OH}{\overset{OH}{\diagdown}} \xrightarrow{k_8} CH_3COOH + H^+ \quad \textbf{Fast, Step III}$$

$$\quad E \qquad\qquad\qquad A \qquad\qquad\qquad\qquad (29)$$

The rate of hydrolysis of PAA similarly can be obtained:

$$\left.\frac{dC_C}{dt}\right|_{hydrolysis} = \frac{k_7 k_{6+}}{k_{6-}}[H^+]C_C C_D = k_2[H^+]C_C C_D$$

$$= k_{2obs}C_C C_D \qquad\qquad (30)$$

Thus, the rate of accumulation of PAA in the system is:

$$\frac{dC_C}{dt} = \left.\frac{dC_C}{dt}\right|_{synthesis} - \left.\frac{dC_C}{dt}\right|_{hydrolysis}$$

$$= k_{1obs}C_A C_B - k_{2obs}C_C C_D \qquad\qquad (31)$$

This equation is actually our initial kinetic Eq. (5). Thus, the above presumed schemes are in accordance with our kinetic results. Therefore, it has been proved that the rate-determining step in the synthesis of PAA is the reaction between H_2O_2 with active carbonyl intermediary, and in the hydrolysis of PAA the reaction between water and corresponding active carbonyl intermediary. Sawaki and Ogata also obtained the same conclusion [18].

4. Conclusions

A homogeneous kinetic model for peracetic acid (PAA) preparation from acetic acid (AA) and hydrogen peroxide (HP) was developed on the basis of some proper postulations. The synthesis and hydrolysis of PAA are both acid-catalyzed processes. The synthesis of PAA is first-order with respect to AA concentration, HP concentration and H^+ concentration. Similarly, the hydrolysis of PAA in acid environment is first order with respect to PAA concentration, water concentration and H^+ concentration. Linear relationships were found between the observed rate constants and H^+ concentrations at a certain temperature, with the slopes being corresponding intrinsic rate constants. The intrinsic activation energies of PAA synthesis and hydrolysis from the corresponding Arrhenius plots are 57.8 and 60.4 kJ mol^{-1}, respectively. Therefore, the kinetic equations for the preparation of PAA from AA and HP under the catalysis of sulfuric acid are as follows:

$$\frac{dC_{PAA}}{dt} = 6.83 \times 10^8 \exp\left(-\frac{57846.15}{RT}\right)$$

$$\times [H^+](C_{AA0} - C_{PAA})C_{HP} - 6.73 \times 10^8$$

$$\times \exp\left(-\frac{60407.78}{RT}\right)[H^+]C_{PAA}(C_{H_2O0} + C_{PAA})$$

$$\frac{dC_{HP}}{dt} = 6.73 \times 10^8 \exp\left(-\frac{60407.78}{RT}\right)$$

$$\times [H^+]C_{PAA}(C_{H_2O0} + C_{PAA}) - 6.83 \times 10^8$$

$$\times \exp\left(-\frac{57846.15}{RT}\right)[H^+](C_{AA0} - C_{PAA})C_{HP}$$

where C_{PAA} and C_{HP} are the concentrations of PAA and HP, and C_{AA0} and C_{H_2O0} are the initial concentrations of AA and water, respectively. It has been shown that the present kinetic equations can well describe our experimental data. It has been proved that the rate-determining step in synthesis of PAA is the reaction between H_2O_2 with active carbonyl intermediary, and in the hydrolysis of PAA the reaction between water and corresponding active carbonyl intermediary.

References

[1] L.B. Brasileiro, J.L. Colodette, D. Pilo-Veloso, Quim. Nova 24 (2001) 819–829.
[2] R. Gehr, M. Wagner, P. Veerasubramanian, P. Payment, Water Res. 37 (2003) 4573–4586.
[3] M. Kitis, Environ. Int. 30 (2004) 47–55.
[4] Y. Cai, S.K. David, Text. Res. J. 67 (1997) 459–464.
[5] Z. Yuan, Y. Ni, A.R.P. Van Heiningen, Appita J. 51 (1998) 377–380.
[6] Q. Yang, F. Tang, Y. Zhang, China Pulp Pap. 22 (2003) 5–8.
[7] P. Krizman, F. Kovac, F.T. Petra, Color. Technol. 121 (2005) 304–309.
[8] D.H. Stormont, Oil Gas J. 58 (1960) 78–79.
[9] R.L. Musante, R.J. Grau, M.A. Baltanas, Appl. Catal. A: Gen 197 (2000) 165–173.
[10] Z. Yuan, Y. Ni, A.R.P. Van Heiningen, Can. J. Chem. Eng. 75 (1997) 37–41.
[11] J.A. John, F.J. Weymouth, Chem. Ind. 2 (1962) 62–69.
[12] C. Wang, R. Fang, Chin. J. Disinf. 23 (2006) 100–102.
[13] L.V. Dul'neva, A.V. Moskvin, Russ. J. Gen. Chem. 75 (2005) 1125–1130.
[14] V.G. Kharchuk, L.A. Petrov, I.P. Kolenko, J. Appl. Chem. USSR 58 (1985) 1228–1232.
[15] E. Koubek, The kinetics and the mechanism of the decomposition of aliphatic peroxyacids in aqueous solutions, Ph.D thesis, Brown University, New York, 1964.
[16] L. Kunigk, D.R. Gomes, F. Forte, K.P. Vidal, L.F. Gomes, P.F. Sousa, Braz. J. Chem. Eng 18 (2001) 217–220.
[17] J.F. Kadla, H.-M. Chang, ACS Symp. Ser. 785 (2001) 108–128.
[18] Y. Sawaki, Y. Ogata, Bull. Chem. Soc. Jap. 38 (1965) 2103–2106.
[19] M. Rubio, G. Ramírez-Galicia, L. Jovany López-Nava, J. Mol. Struc.-THEOCHEM 726 (2005) 261–269.
[20] C.A. Bunton, T.A. Lewis, D.L. Llewellyn, J. Am. Chem. Soc. 78 (1956) 1226.