

Microcalorimetric Investigation on the Kinetics of the Oxidation of Ascorbic Acid with Hydrogen Peroxide

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Based on the thermokinetic theory, a novel thermokinetic research method—self-function regression method, which could be used to determine the kinetic parameters k_1 , k_2 and k_{-1} of the complex reaction: $B + C \xrightleftharpoons[k_{-1}]{k_1} I \xrightarrow{k_2} P$, was proposed in this paper. The kinetics of the reaction of ascorbic acid (H_2A) with hydrogen peroxide was investigated at $pH=5-7$ and $T=298.15$ K, and the kinetic parameters k_1 , k_2 and k_{-1} were obtained with this method. The kinetics of the reaction was investigated in detail. The kinetic parameters of the oxidation of ascorbic monoanion (HA^-) and ascorbic dianion (A^{2-}) with hydrogen peroxide were $3.33 \times 10^{-3} s^{-1}$ and $25.48 s^{-1}$ at 298.15 K, respectively. The molar enthalpy change for the reaction was $-554.64 kJ \cdot mol^{-1}$ in phosphate buffer solution at pH 7 and at 298.15 K.

Keywords ascorbic acid, thermokinetics, self-function regression method, complex reaction, reversible-consecutive first-order reaction

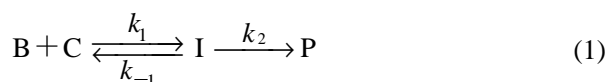
Introduction

Ascorbic acid is still attractive due to its wide-ranging role in biological processes and chemical fields. Consequently the knowledge of the kinetics of ascorbate reduction is highly desirable. In previous papers,¹⁻¹¹ spectroscopy and electronics methods were generally used to study the oxidation of ascorbic acid, and only a first-order reaction rate constant was obtained by these methods. Since the reaction is a complicated process involving several reactive species, the previous studies were still not enough. Based on thermokinetic theory, the self-function regression method, which could be used to determine the kinetic parameters of complex reactions, was proposed and discussed in detail in this paper. The oxidation of ascorbic acid by hydrogen peroxide in buffer solution was also investigated with conduction calorimeter.

Theory and method

Thermokinetic research method for the reversible-consecutive first-order reaction

Analytical equation of thermoanalytical curve of the reversible-consecutive first-order reaction A reversible-consecutive reaction can be expressed as:



where B and C are the reactants; I, P are the intermediate and the product, respectively; k_1 , k_{-1} are the rate constants of the forward reaction and the backward reaction for the first step reaction, respectively; k_2 is the rate constant of the second step.

Tian's equation is generally used in heat conduction calorimeter¹²⁻¹⁵

$$\Delta \frac{d\Delta}{dt} + K\Delta = \Omega \quad (2)$$

and the total heat power Ω of reaction system is

$$\Omega = -V(\Delta H_1 r_1 + \Delta H_2 r_2) \quad (3)$$

where Δ is the height of thermoanalytical curve, and it is proportional to the temperature difference between the reaction system and the surroundings; Δ , K are constants of thermokinetic system. r_1 , r_2 are the reaction rates for the first and second step, respectively; V is the volume of reaction system; ΔH_1 , ΔH_2 are the molar enthalpy changes of the first and the second step reactions, respectively.

If only B and C are present at the beginning of reaction in a sample cell and the initiating concentration of B is far in excess of that of C, $B_0 \gg C_0$, according to the theoretical basis of chemical reaction kinetics and thermokinetics, the analytical equation of thermoanalytical curve of the reversible-consecutive first-order reaction

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can be proved that

$$\Delta = C_1 e^{-\lambda_1 t} + C_2 e^{-\lambda_2 t} + C_3 e^{-kt} \quad (4)$$

where

$$C_1 = \frac{\lambda_1 C_0 V (\lambda_2 \Delta H_1 + \lambda_2 \Delta H_2 - k_1 B_0 \Delta H_1)}{\Lambda (k - \lambda_1) (\lambda_1 - \lambda_2)},$$

$$C_2 = \frac{\lambda_2 C_0 V (\lambda_1 \Delta H_1 + \lambda_1 \Delta H_2 - k_1 B_0 \Delta H_1)}{\Lambda (k - \lambda_1) (\lambda_2 - \lambda_1)},$$

$$C_3 = -(C_1 + C_2), \quad k = \frac{K}{\Lambda} \quad (5)$$

and

$$\lambda_1 = \frac{1}{2} \left\{ (k_1 B_0 + k_2 + k_{-1}) + [(k_1 B_0 + k_2 + k_{-1})^2 - 4k_1 B_0 k_2]^{\frac{1}{2}} \right\} \quad (6)$$

$$\lambda_2 = \frac{1}{2} \left\{ (k_1 B_0 + k_2 + k_{-1}) - [(k_1 B_0 + k_2 + k_{-1})^2 - 4k_1 B_0 k_2]^{\frac{1}{2}} \right\} \quad (7)$$

The self-function regression method for the reversible-consecutive first-order reaction

The mathematical form of the analytical Eq. (4) of the reversible-consecutive first-order reaction is the same as that of the irreversible consecutive first-order reaction taking place in the conduction calorimeter.¹² For a chemical reaction occurring at constant temperature, C_1 and C_2 are constants, therefore the damping constants λ_1 and λ_2 can be calculated according to the method proposed in our previous paper.^{12,13} In this paper, the modification for the self-function regression method was suggested as follows.

Supposing Δ_i , Δ_{i+1} and Δ_{i+2} are one group of height values of thermoanalytical curve, which have the same time interval $\Delta t_1 = t_{i+1} - t_i = t_{i+2} - t_{i+1}$, and Δ_j , Δ_{j+1} , Δ_{j+2} are the other group of height values which have the same time interval Δt_1 , and the time interval between the i -group and the j -group is Δt_2 . $\Delta t_2 = t_j - t_i = t_{j+1} - t_{i+1} = t_{j+2} - t_{i+2}$, then from Eq. (4) it can be proved that

$$\Delta_i = (\alpha + \beta) \Delta_{i+1} - \alpha \beta \Delta_{i+2} + \gamma \Delta_j - \gamma (\alpha + \beta) \Delta_{j+1} + \alpha \beta \gamma \Delta_{j+2} \quad (8)$$

Rearrangement of Eq. (8) leads to

$$\Delta_i - \gamma \Delta_j = (\alpha + \beta) (\Delta_{i+1} - \gamma \Delta_{j+1}) - \alpha \beta (\Delta_{i+2} - \gamma \Delta_{j+2}) \quad (9)$$

$$\text{where} \quad \alpha = e^{\lambda_1 \Delta t_1}, \quad \beta = e^{\lambda_2 \Delta t_1}, \quad \gamma = e^{k \Delta t_2} \quad (10)$$

In Eqs. (8) and (9), Δ_i , Δ_{i+1} , Δ_{i+2} , Δ_j , Δ_{j+1} , Δ_{j+2} are all thermoanalytical curve data, hence the three unknown values of α , β and γ can be calculated. Therefore the parameters λ_1 and λ_2 can be calculated.

Calculation of the kinetic parameters k_1 , k_2 and k_{-1} for reversible-consecutive first-order reaction
From Eqs. (6) and (7), we have

$$\lambda_1 + \lambda_2 = k_1 B_0 + k_2 + k_{-1} \quad (11)$$

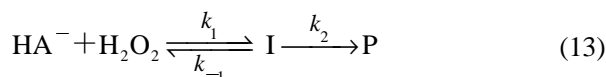
$$\lambda_1 \cdot \lambda_2 = k_1 B_0 \cdot k_2 \quad (12)$$

From Eqs. (11) and (12) it can be seen that $\lambda_1 + \lambda_2$ and $\lambda_1 \cdot \lambda_2$ are linear with B_0 , therefore the kinetic parameters k_1 , k_2 and k_{-1} in model (1) can be obtained by least square method from a series of λ_1 , λ_2 and corresponding B_0 .

Thermokinetic studies for the reaction of ascorbic acid with hydrogen peroxide

The simplified model (Eq. (13)) The process for ascorbic acid oxidized to dehydroascorbic acid (A) is complex. H_2A/HA^- can undergo a reversible Michaelis two-step oxidation-reduction process with the formation of a free radical $A^{\cdot-}$ as an intermediate.⁴ Ascorbic acid has two pK_a values (4.04 and 11.34)³ for successive ionizations in aqueous solution.

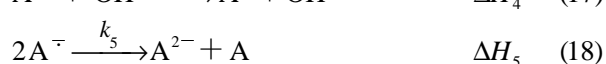
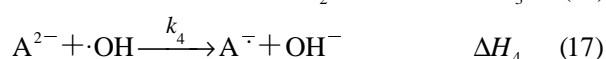
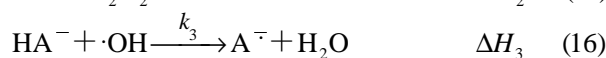
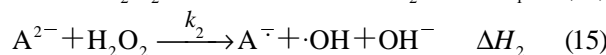
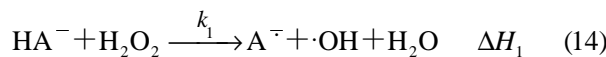
Thus HA^- is the dominant form and the predominant reactive species at $pH=5-7$.^{5,8,9} So the oxidation process may be simplified to



If the concentration of H_2O_2 is far in excess of that of ascorbic acid, $c_{H_2O_2} \gg c_{H_2A}$, the process (13) can be treated as the reversible-consecutive first-order reaction and the parameters λ_1 and λ_2 can be obtained. From Eqs. (11) and (12), the rate constants k_1 , k_2 and k_{-1} can be calculated by least square method. In Eqs. (11) and (12), $B_0 = c_{H_2O_2}$.

The detailed analysis of the reaction of ascorbic acid with hydrogen peroxide

To account for the pH effect, further detailed mechanism of the reaction must be taken into consideration. In fact HA^- and A^{2-} are all important reductants in the range of $pH=5-7$. And free radicals $A^{\cdot-}$ and $\cdot OH$ will be involved in the reaction.



where $\Delta H_1, \Delta H_2, \Delta H_3, \Delta H_4, \Delta H_5$ are the molar enthalpies of reactions (14)–(18), respectively. In this work only the ascorbic acid and hydrogen peroxide were present in the sample cell at the beginning of the reactions and the initiating concentration of hydrogen peroxide was far in excess of that of ascorbic acid, $c_{\text{H}_2\text{O}_2} \gg c_{\text{H}_2\text{A}}$; because the $\cdot\text{OH}$ is a very reactive free radical in reaction, it can be treated with steady-state theory, $d[\cdot\text{OH}]/dt=0$; A^- is relatively unreactive toward other chemical compounds,⁴ so its concentration may be treated as constant c_0' to some extent; and if assuming $k_3[\text{HA}^-] \gg k_4[\text{A}^{2-}]$, the thermoanalytical curve equation of the reaction of the ascorbic acid with hydrogen peroxide can be deduced based on the chemical kinetics and the above-stated theory.

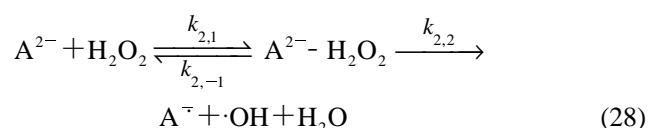
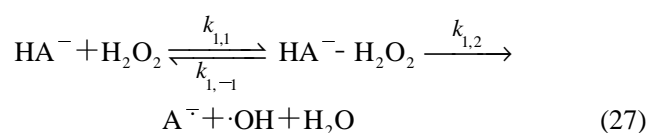
$$\left. \begin{aligned} D_1 &= \frac{VC_{\text{H}_2\text{O}_2}C_{\text{H}_2\text{A}}}{\Lambda(\lambda_1-k)(\lambda_1-\lambda_2)} \left[\left(\frac{k_1}{\theta_1}\Delta H_1 + \frac{k_1}{\theta_1}\Delta H_3 + \frac{k_2}{\theta_2}\Delta H_2 + \frac{k_2}{\theta_2}\Delta H_3 + \frac{k_1k_4}{\theta_2k_3}\Delta H_4 + \frac{\theta_1k_2k_4}{\theta_2^2k_3}\Delta H_4 \right) \right. \\ &\quad \left. \left(2\frac{k_1}{\theta_1}c_{\text{H}_2\text{O}_2} + 2\frac{k_2}{\theta_2}c_{\text{H}_2\text{O}_2} - \lambda_2 \right) + \frac{k_5c_0'}{\theta_1}\Delta H_5 \left(2\frac{k_1}{\theta_1} + 2\frac{k_2}{\theta_2} \right) \right] \\ D_2 &= \frac{VC_{\text{H}_2\text{O}_2}c_{\text{H}_2\text{A}}}{\Lambda(\lambda_2-k)} \left[\frac{k_1\Delta H_1}{\theta_1} + \frac{k_1\Delta H_3}{\theta_1} + \frac{k_2\Delta H_2}{\theta_2} + \frac{k_2\Delta H_3}{\theta_2} + \frac{k_4}{\theta_2k_3} \left(k_1 + k_2\frac{\theta_1}{\theta_2} \right) \Delta H_4 + \frac{D_1\Lambda(k-\lambda_1)}{VC_{\text{H}_2\text{O}_2}c_{\text{H}_2\text{A}}} \right] \\ D_3 &= -(D_1 + D_2) \end{aligned} \right\} \quad (24)$$

In this work every reaction occurred in the buffer solution at constant temperature. Hence $\Delta H_1, \Delta H_2, \Delta H_3, \Delta H_4, \Delta H_5, \theta_1, \theta_2, \lambda_1$ and λ_2 were all constants for each reaction. Consequently D_1 and D_2 were also constants. According to above-stated method, the constants λ_1, λ_2 can be calculated from Eq. (19).

$$\text{let } \frac{2k_1c_{\text{H}_2\text{O}_2}}{\theta_1} + \frac{2k_2c_{\text{H}_2\text{O}_2}}{\theta_2} = k' \quad (25)$$

$$k_5c_0' = k_5' \quad (26)$$

According to Eqs. (20), (21), (25) and (26), k' and k_5' can be obtained from λ_1 and λ_2 . That k' is varied really with $c_{\text{H}_2\text{O}_2}$ and that $\frac{1}{k'}$ is linear with $\frac{1}{c_{\text{H}_2\text{O}_2}}$ indicate that the complex $\text{HA}^- \cdot \text{H}_2\text{O}_2 / \text{A}^{2-} \cdot \text{H}_2\text{O}_2$ may be formed in the reaction, hence Eqs. (27) and (28) could be substituted instead of Eqs. (14) and (15).



According to Eqs (27) and (28), Eq. (29) should be

$$\Delta = D_1e^{-\lambda_1 t} + D_2e^{-\lambda_2 t} + D_3e^{-kt} \quad (19)$$

$$\text{where } \lambda_1 + \lambda_2 = \frac{2k_1c_{\text{H}_2\text{O}_2}}{\theta_1} + \frac{2k_2c_{\text{H}_2\text{O}_2}}{\theta_2} + 2k_5c_0' \quad (20)$$

$$\lambda_1 \cdot \lambda_2 = \left(\frac{2k_1c_{\text{H}_2\text{O}_2}}{\theta_1} + \frac{2k_2c_{\text{H}_2\text{O}_2}}{\theta_2} \right) \cdot 2k_5c_0' \quad (21)$$

$$\theta_1 = 1 + \frac{[\text{H}^+]}{K_{a_1}} + \frac{K_{a_2}}{[\text{H}^+]} \quad (22)$$

$$\theta_2 = 1 + \frac{[\text{H}^+]}{K_{a_2}} + \frac{[\text{H}^+]^2}{K_{a_1}K_{a_2}} \quad (23)$$

substituted for Eq. (25)

$$k' = \frac{2k_{1,2}c_{\text{H}_2\text{O}_2}}{\theta_1(K_{m_1} + c_{\text{H}_2\text{O}_2})} + \frac{2k_{2,2}c_{\text{H}_2\text{O}_2}}{\theta_2(K_{m_2} + c_{\text{H}_2\text{O}_2})} \quad (29)$$

where $K_{m_1} = \frac{k_{1,-1} + k_{1,2}}{k_{1,1}}$, $K_{m_2} = \frac{k_{2,-1} + k_{2,2}}{k_{2,1}}$. If the equilibriums of the first step in Eqs. (27) and (28) can reach rapidly, the $\frac{1}{K_{m_1}}$ and $\frac{1}{K_{m_2}}$ will be the associated constants of H_2O_2 with HA^- and A^{2-} , respectively. Assuming $K_{m_1} = K_{m_2} = K_m$, Eq. (29) becomes into

$$k' = \frac{2k_{1,2}c_{\text{H}_2\text{O}_2}}{\theta_1(K_m + c_{\text{H}_2\text{O}_2})} + \frac{2k_{2,2}c_{\text{H}_2\text{O}_2}}{\theta_2(K_m + c_{\text{H}_2\text{O}_2})} \quad (30)$$

$$\text{let } \frac{2k_{1,2}}{\theta_1} + \frac{2k_{2,2}}{\theta_2} = k'' \quad (31)$$

Rearranging Eq. (30), we have

$$\frac{1}{k'} = \frac{1}{k''} + \frac{K_m}{k''c_{\text{H}_2\text{O}_2}} \quad (32)$$

Eq. (32) shows that $\frac{1}{k'}$ is linear with $\frac{1}{c_{\text{H}_2\text{O}_2}}$. Therefore k'' and K_m can be obtained from the intercept and the slope. Consequently, $k_{1,2}$ and $k_{2,2}$ can be calculated from Eqs. (22), (23) and (31) by using k'' values at different pH.

Enthalpy change of reaction of ascorbic acid with hydrogen peroxide

Integrating Eq. (2) with respect to time from 0 to ∞ , we obtain

$$KA = Q_{\infty} \quad (33)$$

where A is the total area under thermoanalytical curve, and Q_{∞} is the total heat effect for a reaction. K can be obtained by electric calibration,¹⁵ therefore the Q_{∞} can be calculated from the area A . Consequently the reaction enthalpy change ΔH_m can be determined from Q_{∞} and the quantity of the reacted ascorbic acid.

Experimental

Reactants

Ascorbic acid, 30% hydrogen peroxide, sodium hydroxide, potassium diphosphate, potassium hydrogen phthalate were all of analytical purity. The buffer solutions at pH values below 7 for the experiments were prepared by using potassium hydrogen phthalate and sodium hydroxide and the buffers of pH=7 were prepared by using potassium diphosphate and sodium hydroxide. The ionic strength was maintained at 0.12 (KCl). The concentration of hydrogen peroxide was standardized with potassium permanganate.

Calorimetric measurement

All the thermoanalytical curves of the reactions were measured with a twin conduction calorimeter at 298.15 K. The calorimeter construction and the operation way have been described in detail in previous articles.^{14,15}

UV-spectrophotometric measurement

UV kinetic measurement was made spectrophoto-

metrically at 298.15 K, employing a Shimadzu UV2100 spectrophotometer with a thermostatic cell compartment. The reactions were initiated by adding 5 μ L of 0.3 mol/L ascorbic acid solution into 3 mL of buffer solution containing the desired reagents. For pH = 5 buffer solution, the absorbance A_t was recorded by monitoring the formation of product at 330 nm vs. time. For pH = 7 buffer solution, the absorbance A_t was recorded by monitoring the disappearance of ascorbic acid at 286 nm vs. time. The λ_1 and λ_2 can be obtained from different time course with Fersht's method¹⁶ (The evaluated values are labeled with * in Table 1). λ_1 and λ_2 can be also obtained with the following method: According to the theory of chemical reaction kinetics, we have $A_t - A_{\infty} = B_1 e^{-\lambda_1 t} + B_2 e^{-\lambda_2 t}$, where B_1 and B_2 were constants at constant temperature, and A_{∞} was the final absorbance. Thus the values of λ_1 and λ_2 can be calculated by using the self-function regression method¹³ (The evaluated values are labeled with ** in Table 1).

Results and discussion

Stoichiometry

The stoichiometric relation between ascorbic acid and hydrogen peroxide was investigated in our work, and the following stoichiometric equation was found



The 1 : 1 stoichiometric relationship of hydrogen peroxide to ascorbic acid was in agreement with Ghosh's work (1.03 : 1).⁶

Reaction kinetics

Ascorbic acid has two $\text{p}K_a$ values in aqueous solution, one at 4.04 and the other at 11.34.³ Hence HA^-

Table 1 Kinetic damping constants λ_1 and λ_2 for the oxidation of H_2A by H_2O_2 in buffer solutions with different pH value ($T=298.15$ K, $\mu=0.12$)

pH	$c_{\text{H}_2\text{O}_2} / (\text{mol} \cdot \text{L}^{-1})$	$10^3 c_{\text{H}_2\text{A}} / (\text{mol} \cdot \text{L}^{-1})$	$10^3 \lambda_1 / \text{s}^{-1}$			$10^4 \lambda_2 / \text{s}^{-1}$		
5	0.3078	11.54	2.974	3.81*	3.72**	3.390	3.3*	2.0**
	0.4615	11.54	3.532			4.223		
	0.7692	11.54	4.531	4.28*	6.01**	5.521	5.16*	5.29**
6	0.1538	11.54	3.943			4.054		
	0.3078	11.54	4.706			5.505		
	0.4615	11.54	5.557			4.343		
	0.7692	11.54	7.798			5.209		
7	0.0462	2.282	3.678			2.805		
	0.0462	4.465	3.533			2.550		
	0.0923	4.565	4.310			1.860		
	0.1538	11.54	5.570			4.450		
	0.7692	11.54	12.24			8.470		

* The values evaluated with Fersht's method¹⁶ from UV-spectrophotometry, $c_{\text{H}_2\text{A}} = 5 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$. ** The values evaluated with self-function regression method¹³ from UV-spectrophotometry, $c_{\text{H}_2\text{A}} = 5 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$.

will be the dominant form in the range of pH=5–10, and may be the predominant reductive species because of its concentration advantage.^{5,8,9} Thus, Eq. (13) was reasonable model of the reaction. Based on the simplified model, the kinetic parameters k_1 , k_2 and k_{-1} can be calculated from Eqs. (11) and (12), and the results are listed in Tables 1 and 2. From Table 2 it can be seen that the values of k_2 at different pH were almost close to each other, and the average was $9.39 \times 10^{-4} \text{ s}^{-1}$, while the values of k_1 and k_{-1} varied obviously with pH. The pH effect clearly indicates that HA^- and A^{2-} are the important reactive species for the oxidation of ascorbic acid. Therefore Scheme 1 would be the more reasonable model of the reaction mechanism. From Table 3 it can be estimated that $k_5' \sim 10^{-4} \text{ s}^{-1}$, so the value of concentration of free radical A^\cdot , *ca.* 10^{-9} mol/L , was evaluated from $k_5 = 2.4 \times 10^5 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$,³ and it was in agreement with the investigation ($[\text{A}^\cdot] < 10^{-8} \text{ mol/L}$ = by Skurlatov with ESR.¹ From Table 4 it can be seen that the rate constants of the reaction of HA^- and A^{2-} with hydrogen peroxide were $3.33 \times 10^{-3} \text{ s}^{-1}$ and 25.48 s^{-1} , respectively. The great difference may be explained from the greatly different redox potential ($E_{\text{HA}^-/\text{HA}^-}^0 = 0.723 \text{ V}$ and $E_{\text{A}^{2-}/\text{A}^{2-}}^0 = 0.019 \text{ V}$).³ This

Table 2 Kinetic parameters k_1 , k_2 and k_{-1} for the oxidation of ascorbic acid by H_2O_2 ($T=298.15 \text{ K}$, $\mu=0.12$)

pH	$10^3 k_1/(\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1})$	$10^3 k_2/\text{s}^{-1}$	$10^3 k_{-1}/\text{s}^{-1}$
5	3.812	0.852	1.310
6	6.435	0.889	2.367
7	12.595	1.077	2.402

Table 3 Kinetic parameters k' and k_5' (Scheme 1, $T=298.15 \text{ K}$, $\mu=0.12$)

pH	$c_{\text{H}_2\text{O}_2}/(\text{mol} \cdot \text{L}^{-1})$	$10^3 c_{\text{H}_2\text{A}}/(\text{mol} \cdot \text{L}^{-1})$	$10^3 k'/\text{s}^{-1}$	$10^3 k_5'/\text{s}^{-1}$
5	0.3078	11.54	2.510	4.02
	0.4615	11.54	2.939	5.08
	0.7692	11.54	3.748	6.68
6	0.1538	11.54	3.411	4.68
	0.3078	11.54	3.942	6.57
	0.4615	11.54	5.032	4.80
7	0.7692	11.54	7.189	5.65
	0.0462	2.282	3.341	3.09
	0.0462	4.465	3.230	2.79
	0.0923	4.565	4.105	1.95
	0.1538	11.54	5.029	4.93
	0.7692	11.54	11.23	9.22

study clearly indicates that A^{2-} has the greater reactivity relative to HA^- , and A^{2-} is the kinetically important reductant at pH values above 6. The conclusion is in agreement with that of Williams.³ Additionally, the fact that K_m decreased with pH indicated that ascorbic acid was more liable to associate with hydrogen peroxide in neutral than in acidic solution.

Table 4 Calculated values of k'' , k_m , $k_{1,2}$ and $k_{2,2}$ at 298.15 K , $\mu=0.12$

pH	$10^3 k''/\text{s}^{-1}$	K_m	$10^3 k_{1,2}/\text{s}^{-1}$	$k_{2,2}/\text{s}^{-1}$
5	5.40	0.361	3.33	25.48
6	7.57	0.204		
7	8.91	0.083		

Molar enthalpy change of the reaction

The K value, $8.608 \times 10^{-2} \text{ J} \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, was determined for this reaction system by electric power calibration at 298.15 K . Thus the molar enthalpy change of the reaction of ascorbic acid with hydrogen peroxide, $\Delta H_m = -554.64 \text{ kJ} \cdot \text{mol}^{-1}$ (Table 5), was determined and the reaction was an exothermic process at 298.15 K and $\text{pH}=7$ in phosphate buffer with ionic strength $\mu=0.12$. The relatively large heat effect caused by reaction is due to the formation of two moles of H_2O which has relatively large standard molar enthalpy of formation.

Table 5 Total thermoanalytical curve areas and the molar enthalpy change ΔH_m in phosphate buffer solution ($K=8.608 \times 10^{-2} \text{ J} \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, $T=298.15 \text{ K}$, $\text{pH}=7$, $\mu=0.12$)

$10^2 c_{\text{H}_2\text{O}_2}/(\text{mol} \cdot \text{L}^{-1})$	$10^3 c_{\text{H}_2\text{A}}/(\text{mol} \cdot \text{L}^{-1})$	$A/(\text{V} \cdot \text{s})$	$\Delta_r H_m/(\text{kJ} \cdot \text{mol}^{-1})$
4.615	2.282	947.07	-549.61
4.615	4.565	1935.36	-561.45
9.231	4.565	1905.75	-552.86
Ave.			-554.64

About the self-function regression method

In the previous papers,^{12,13} the self-function regression method for the first-order and for the consecutive first-order reaction was proposed. In this work, this method for the reversible-consecutive first-order reaction was suggested. From Table 1 it can be seen that the values of λ_1 and λ_2 determined by the calorimetric technique were almost approximated to those by the UV spectrophotometry, and that the values of λ_1 and λ_2 evaluated from the data of the UV measurement with the self-function regression method¹³ were also approximated to those with Fersht's method.¹⁶ Therefore the self-function regression method could be applied to the evaluation of kinetic parameters in spectroscopy.

Since several kinetic parameters can be calculated simultaneously only from the data of certain time period

with the self-function regression method, this method could be used to provide kinetic information for complicated processes which show different kinetic qualities in different time period. It is worthy to note that the self-function regression method was particularly suited for the case that the values of those kinetic parameters λ_1 , λ_2 and k approximate to one another and the difference between each other should not be large by 15-fold. Owing to the thermal relaxation phenomenon,¹⁷ Tian's Eq. (2) can not be used for faster reaction. Thus the rate constants studied should be less than 0.03 s^{-1} when conduction calorimeter was used. The time interval Δt_1 and Δt_2 in Eqs. (8)—(10) should be selected at reasonable values, and the values of α , β and γ in Eq. (10) should be in the range from 1.2 to 5, *i.e.* $1.2 < \alpha$ (or β , or γ) < 5 . In this work, Δt_1 values were selected from 300 to 800 s and Δt_2 from 100 to 300 s, respectively.

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