CALORIMETRY STUDIES OF A CHEMICAL OSCILLATORY SYSTEM
The effect of putrescine on KSCN–H₂O₂–CuSO₄–NaOH reactions

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The effect of putrescine (PUT) on KSCN–H₂O₂–CuSO₄–NaOH oscillating system was investigated by calorimetric method. The oscillating reaction was monitored in a closed reactor with stirring, and the result showed that the oscillating period was linearly related with putrescine concentration and the numbers of oscillation decreased with increase in putrescine concentration. When [PUT]=$2.83 \cdot 10^{-4}$ M, no oscillation was observed. A possible mechanism is proposed that putrescine is a scavenger of the active-oxygen species. The result of numerical simulation by a simplified mechanism consisting of 18 kinetic steps and 16 variables is consistent with the experimental findings.

Introduction

Since the first homogeneous liquid-phase chemical oscillation began [1] about eighty years ago, reaction families based on oxyhalogen species have dominated the fields. But only recently has progress been made in finding halogen-free chemical oscillators, such as S^{2-}–H_2O_2 [2], $S_2O_3^{2-}$–H_2O_2 [3] and KSCN–H_2O_2–CuSO₄–NaOH [4], and so on. Among these, the KSCN–H_2O_2–CuSO₄–NaOH system, which can oscillate under batch as well as under flow conditions, exhibits the complex dynamic behavior, including slowly damped oscillation in color and oxygen evolution.

Of the large variety of experimental methods including potentiometric [5] and spectroscopic methods [6, 7] used to reveal the 'secrets' of temporal as well as spatial periodicities, calorimetric method [8] used for studying on the oscillating system is reported rarely. Actually it is also an informative one [9, 10] for unspecific, non-invasion and insensitive to the electrochemical and optical properties of the investigated system. It could be demonstrated that in oscillatory reactions the rate of heat production is periodic and the temperature rises in a stepwise manner, and these appear synchronized with the concentration oscillations of the reaction intermediates.

In this paper the effect of putrescine on the KSCN–H₂O₂–CuSO₄–NaOH system in closed conditions was investigated by calorimetry method and a simplified mechanism consisting of 18 kinetic steps and 16 variables was presented to explain the experiment

results. Putrescine, which is an aliphatic nitrogenous base with low molecular mass, is a kind of polyamines and exists in almost every organism. Polyamine can scavenge of the active-oxygen free radicals, such as $HO_2 \cdot$, $HO \cdot$ and $O_2 \cdot$ in a direct way [11, 12] and in an indirect [13, 14] way by activating antioxygenic enzymes e.g. superoxide dismutase (SOD), catalase (CAT) and peroxidase (POD), etc. Here, we put it into the KSCN–H₂O₂–CuSO₄–NaOH system that involves active-oxygen free radicals to investigate its function.

Experimenta

Reagents

Stock solutions of KSCN, NaOH and CuSO₄ were prepared using analytical grade chemicals dissolved in doubly distilled water. The concentrations of KSCN, NaOH and H₂O₂ were titrated with standard AgNO₃, potassium acid phthalate and KMnO₄, respectively. Putrescine (PUT) was purchased from Tokyo Kasei Kogyo Co., Ltd., Tokyo, Japan. All other chemicals were of reagent grade and commercially available.

Calorimetric experiments

Apparatus

Calorimetric experiments were performed by using a self made isoperibol calorimeter [15] consisting of three sections: thermostatic apparatus, reaction apparatus

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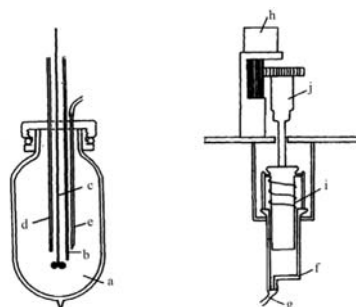
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Fig. 1 Schematic diagram of reaction apparatus; a–calorimeter vessel, b–thermistor, c–stirrer, d–electric heater, e–access capillary, f–syringe, g–silicone tube, h–stepper motor, i–spring, j–amesdial

Fig. 2 Typical calorimetric profiles for the oscillating reaction in the absence of PUT. a–Q–t curve and b–differential curve (dQ/dt–t curve). The initial concentrations are: [KSCN], 0.025 M; [H$_2$O$_2$], 0.204 M; [NaOH], 0.0257 M; [CuSO$_4$], 2.00·10^{-4} M (303.15 K)

(Fig. 1) and temperature measurement apparatus. The calorimetric vessel is a silvered vessel of 100 cm^3 internal volume with one inlet at the top, equipped with an electrical stirring, one resistor for the electric calibration of the apparatus and one thermistor for measuring the temperature of reaction system. The resolution of temperature is 0.0001 K. Thermal inertial time of the thermistor is 4 s. The inlet of calorimetric vessel is connected with a sample injector, which has a maximal volume of 5 mL and controlled by a stepper motor with a precision of 0.002 mL. The reaction apparatus is immersed in a water thermostat at 30.000±0.001°C. The accuracy and precision of the calorimeter were evaluated by determining the heat of protonation of trihydroxymethyl-aminomethane (THAM) by HCl, the value of which was –47.567±0.08 kJ mol^{-1}. This gives a good agreement with the reference value, –47.61 kJ mol^{-1} [16].

Methods

In the experiment, the calorimetric vessel was filled with 100 mL KSCN, NaOH and CuSO$_4$ solutions and the final concentrations were 0.025, 0.0257, 2.00·10^{-4} M respectively. The sample injector was filled with H$_2$O$_2$ solution. After the baseline was steady, H$_2$O$_2$ was injected into the calorimetric vessel and then the reactions were initiated. The final concentration of H$_2$O$_2$ titrated was 0.204 M. Putrescine over a range of concentration from 0–2.83·10^{-4} M was used to investigate its effect on this oscillating system, and was prepared by adding certain volume of putrescine in the calorimetric vessel just before the experiment. The reactant mixtures were stirred electrically at 375 rpm, to ensure thorough mixing. The experimental temperature was conducted at 303.15 K. The calorimetric
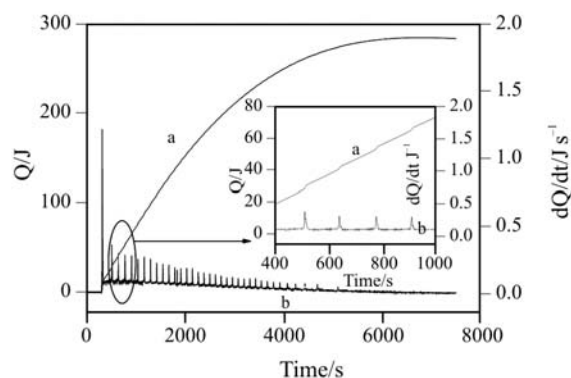
signal was recorded by a digital multimeter (UT70D, You De Li science and technology corporation, China) with the precision of 0.001 mv at an interval of one second.

Results and discussion

The effect of reaction variables

After H$_2$O$_2$ was added, the reaction solution turned into an intense yellow color. The heat output seemed to change exothermically dramatically at first, but after an about 4-min-induction period it exhibited a slow increase in a stepwise manner. Figure 2 shows a typical calorimetric oscillation profile in the absence of PUT, and it can be easily seen that the oscillations have lasted for almost two hours and the number of oscillation is approximately thirty times. With the time going, the oscillating period increases and the amplitude decreases gradually. A large exothermicity accompanies the whole process in which the change of temperature was about 2.5°C. The process was also accompanied by oscillations in color between dark yellow and pale yellow and finally nearly colorless. Since our experiment was conducted in a closed condition, the oscillations appeared in the form of damping and were aperiodic strictly speaking. So the oscillating period (t_p) was defined as an average period over three oscillations, which were nearly closed to the initial concentrations of the reactants.

The system was optimized by changing each variable in turn while keeping all other constant in the absence of PUT. The optimizing of these variables was carried out with two criteria in mind, namely: (a) it can exhibit

Table 1 The initial concentration range of the reactants and temperature range in the oscillating system (concentration unit: mol dm^{-3})

[KSCN]	[H$_2$O$_2$]	[CuSO$_4$]	[NaOH]	Temperature/K
0.0048–0.0238	0.103–0.302	4.0·10^{-5}–2.0·10^{-4}	0.0077–0.0257	298.15–308.15

Fig. 3 Calorimetric profiles of oscillation at different [H₂O₂]. The initial concentrations are: [KSCN], 0.025 M; [NaOH], 0.0257 M; [CuSO₄]₀, 2.00·10⁻⁴ M; [H₂O₂], a–0.103, b–0.153, c–0.204, d–0.253, e–0.302 M (303.15 K)
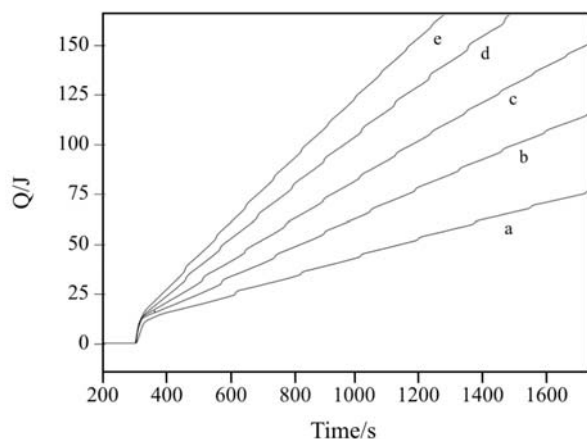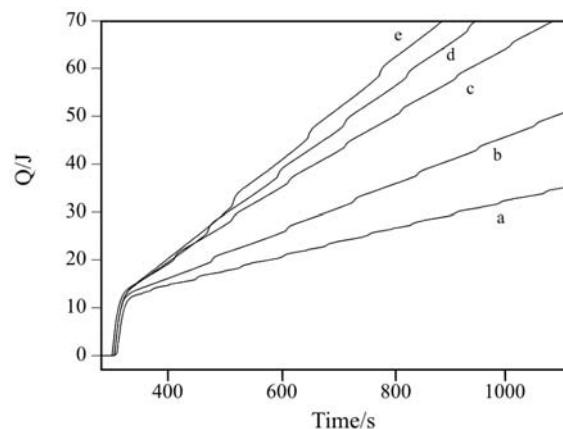
Fig. 3 Calorimetric profiles of oscillation at different $[H_2O_2]$. The initial concentrations are: [KSCN], 0.025 M; [NaOH], 0.0257 M; $[CuSO_4]_0$, $2.00 \cdot 10^{-4}$ M; $[H_2O_2]$, a–0.103, b–0.153, c–0.204, d–0.253, e–0.302 M (303.15 K)

Fig. 4 Calorimetric profiles of oscillation at different [KSCN]. The initial concentrations are: [NaOH], 0.0257 M; $[CuSO_4]$, $2.00 \cdot 10^{-4}$ M; $[H_2O_2]$, 0.204 M; [KSCN] a–0.00476, b–0.0095, c–0.0143, d–0.0191, e–0.0238 M (303.15 K)

obvious oscillating amplitude, which ensures higher sensitivity for the following determination of effect of PUT; (b) the oscillation period is easy to be determined.

Table 1 gives the initial concentration range of the reactants and the temperature range in the oscillating system. Figure 3 gives the effect of H_2O_2 on the oscillation. The oscillation period decreases and the output heat increases with the increase of the concentration of H_2O_2. Figure 4 gives the effect of KSCN on the oscillation. The oscillation period and the output heat increase with the increase of KSCN. And the effect of temperature on the oscillation is shown in Fig. 5. A very good linear relationship was obtained when fitting $\ln t_p$ *vs.* T^{-1}, with the linear correlation coefficient of 0.996. According to Arrhenius equation,

$$\ln t_p = E_a / R(1/T) + A$$

where E_a is the apparent activation energy, A is the intercept, the value of E_a is 45.85 kJ mol⁻¹.

The experimental results show:

$$t_p \propto [KSCN] \ln(1/[H_2O_2])[CuSO_4]^{-1} \cdot$$
$$\cdot f[NaOH] \exp(45.85/RT)$$

Among these factors, pH has a complex influence on the oscillation, so the effect of OH⁻ is presented using f[NaOH]. The final concentration selected is: [KSCN], 0.025 M; $[H_2O_2]$, 0.204 M; $[CuSO_4]$, $1.0 \cdot 10^{-4}$ M; [NaOH], 0.0257 M. The temperature is 303.15 K.

The effect of putrescine on the oscillating system

Figure 6 shows the calorimetric and differential profiles of the oscillating system in the presence of different PUT concentrations. It is obvious that the
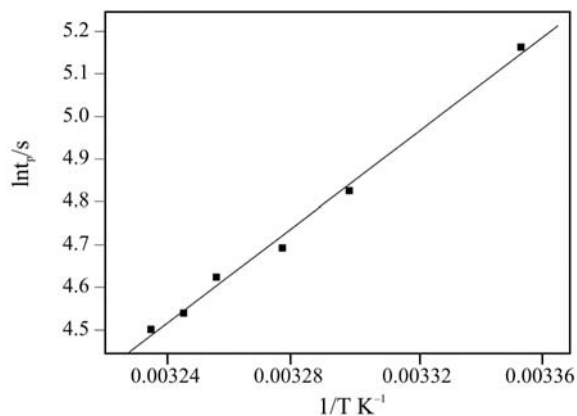

Fig. 5 The effect of temperature on the oscillating system: $\ln t_p$ *vs.* 1/*T*. The initial concentrations are: [KSCN], 0.025 M; $[H_2O_2]$, 0.204 M; $[CuSO_4]$, $2.0 \cdot 10^{-4}$ M; [NaOH], 0.0257 M

oscillation period increases and the number of oscillation decreases with the increase of PUT concentration. When the concentration of PUT equals to $2.83 \cdot 10^{-4}$ M, the oscillation is inhibited completely. The plot of t_p (oscillation period) *vs*. PUT concentration is shown in Fig. 7. The oscillation period is linearly related to PUT concentration, namely: $t_p = 158 + 37.52[\text{PUT}]$ ([PUT]<$2.83 \cdot 10^{-4}$ M), the linear correlation coefficient is greater than 0.996.

Simplification of mechanism of oscillation

Despite many efforts to study on the possibility of analytical applications of chemical oscillation for the determination of the microvolume of analyte [17, 18], the chemical oscillators have so far been mainly studied from a physico-chemical point of view to elucidate the complex reaction mechanisms behind them. However we can put forward a tentative interpretation
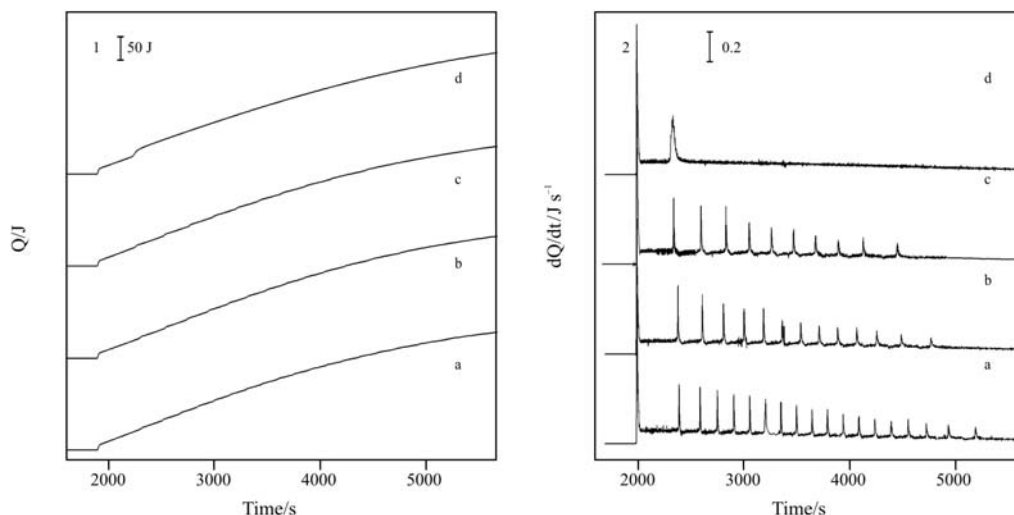
Fig. 6 The 1–calorimetric and 2–differential profiles of oscillation in the presence of PUT. The initial concentrations are: [KSCN], 0.025 M; [H_2O_2], 0.204 M; [NaOH], 0.0257 M; [$CuSO_4$], $1.00\cdot10^{-4}$ M; [PUT], a–$5.65\cdot10^{-5}$, b–$1.13\cdot10^{-4}$, c–$2.26\cdot10^{-4}$, d–$2.83\cdot10^{-4}$ M; (303.15 K)
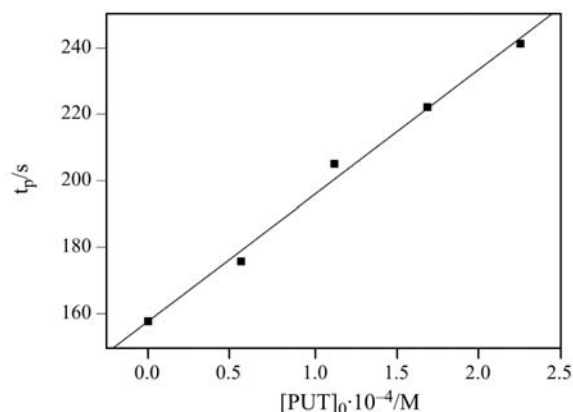
Fig. 7 The effect of the concentration of PUT on the oscillating periods (t_p). The initial concentrations are: [KSCN], 0.025 M; [H_2O_2], 0.204 M; [NaOH], 0.0257 M; [$CuSO_4$], $1.00\cdot10^{-4}$ M (303.15 K)

based on the some of our experimental results and the previous findings of Luo *et al.* [19] With the purpose of using elemental reactions as fewer as possible to elucidate the essential mechanism of oscillating reactions, we select 18 kinetic steps and 16 variables from the 30 kinetic steps and 26 variables in the mechanism recommended by Luo *et al.* The 18 kinetics steps are shown below:
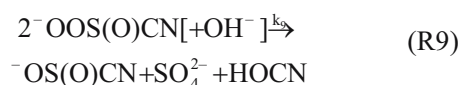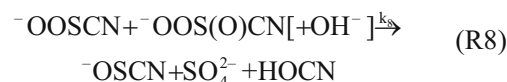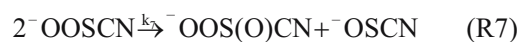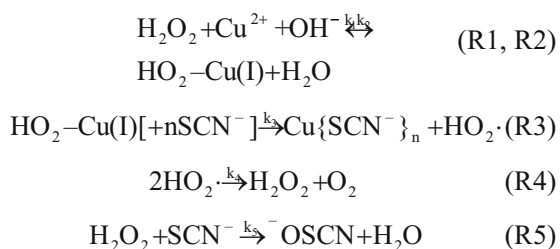
$$H_2O_2 + Cu^{2+} + OH^- \overset{k_1 k_2}{\rightleftharpoons} \qquad (R1, R2)$$
$$HO_2 - Cu(I) + H_2O$$

$$HO_2 - Cu(I)[+nSCN^-] \overset{k_3}{\rightarrow} Cu\{SCN^-\}_n + HO_2\cdot \quad (R3)$$

$$2HO_2\cdot \overset{k_4}{\rightarrow} H_2O_2 + O_2 \qquad (R4)$$

$$H_2O_2 + SCN^- \overset{k_5}{\rightarrow} {}^-OSCN + H_2O \qquad (R5)$$

$$H_2O_2 + {}^-OSCN \overset{k_6}{\rightarrow} {}^-OOSCN + H_2O \qquad (R6)$$

$$2\,{}^-OOSCN \overset{k_7}{\rightarrow} {}^-OOS(O)CN + {}^-OSCN \qquad (R7)$$

$$\begin{aligned}&{}^-OOSCN + {}^-OOS(O)CN[+OH^-] \overset{k_8}{\rightarrow} \\ &{}^-OSCN + SO_4^{2-} + HOCN\end{aligned} \qquad (R8)$$

$$\begin{aligned}&2\,{}^-OOS(O)CN[+OH^-] \overset{k_9}{\rightarrow} \\ &{}^-OS(O)CN + SO_4^{2-} + HOCN\end{aligned} \qquad (R9)$$

$$HOCN + f\,OH^- \overset{k_{10} k_{11}}{\rightleftharpoons} OCN + H_2O \quad (R10,R11)$$

$$\begin{aligned}&{}^-OS(O)CN + {}^-OOS(O)CN + \\ &+ H_2O \overset{k_{12}, k_{13}}{\rightleftharpoons} 2OS(O)CN[+2OH^-]\end{aligned} \qquad (R12,R13)$$

$$\begin{aligned}&\cdot OS(O)CN + Cu + \{SCN^-\}_n \overset{k_{14}}{\rightarrow} \\ &{}^-OS(O)CN + Cu^{2+}\{+nSCN^-\}\end{aligned} \qquad (R14)$$

$${}^-OS(O)CN + HO_2\cdot \overset{k_{15}}{\rightarrow} SO_3^- \cdot + HOCN \qquad (R15)$$

$$\begin{aligned}&SO_3^- \cdot + Cu^+\{SCN^-\}_n \overset{k_{16}}{\rightarrow} \\ &SO_3^{2-}\cdot + Cu^{2+}\{+nSCN^-\}\end{aligned} \qquad (R16)$$

$$2SO_3^-\cdot[+2OH^-] \overset{k_{17}}{\rightarrow} SO_4^{2-} + SO_3^{2-} + H_2O \qquad (R17)$$

$$H_2O_2 + SO_3^{2-} \overset{k_{18}}{\rightarrow} SO_4^{2-} + H_2O \qquad (R18)$$

Indeed, these elemental reactions are derived from two subsystems: H_2O_2–Cu^{2+} and H_2O_2–KSCN. (R1)–(R4) belong to the subsystem of H_2O_2–Cu^{2+}, and (R5)–(R11) belong to the subsystem of H_2O_2–KSCN. (R12)–(R17) are the centerpiece of the mechanism of the oscillating reactions, including the positive (R12)–(R14) and negative (R15)–(R17) feedback loops on which the autocatalytic process relies. The autocatalysis is accomplished by (R12), (R13) and (R14).

Intermediate $^-$OS(O)CN is generated autocatalytically through the formation and reduction of the radical ·OS(O)CN. The Cu^+ is simultaneously oxidized to Cu^{2+} and then the fast equilibrium (R1), (R2), produces the yellow superoxy complex almost immediately if the pH value of system is in appropriate range (pH>9). The yellow superoxy copper(I), HO_2–Cu(I), which is formed in the positive and consumed in the negative feedback loops, plays an important role in the oscillating process. To bring the system back to the previous state, a negative feedback is required. In (R15), the intermediate $^-$OS(O)CN generated autocatalytically is consumed by HO_2· so that it can go back to the previous concentration firstly to initiate the oscillation again. The concentration of $Cu^+\{SCN^-\}_n$ species is crucial for the feedback network. When the concentration of $Cu^+\{SCN^-\}_n$ becomes high enough, it can make the positive feedback significant.

In addition, this mechanism summarizes several reactions about hydroxyl into a non-stochiometric equilibrium reaction (R10), (R11), depending on the parameter, i.e., the stoichiometric factor f. This non-stoichiometric reversible reaction is easy to use but hard to justify, especially as to the exact value of the parameter to be used. OH^- is representatively described to react with HOCN, actually it also reacts with NH_4^+, H_2CO_3.

Compared with the mechanism of Luo *et al.* [19], the reactions of pH<7 are not taken into account in the primary ones. The reasons for this are: firstly, according to the experimental observations, when pH<9, no oscillation appears despite the reactions are still processing. So these are not important but not necessary to initiate an oscillation; Secondly, the results calculated by 26 differential equations show the concentrations of some variables involved in pH<7 such as $Cu(CN)_2(10^{-10}$ M), $Cu(CN)(10^{-14}$ M), OH·$(10^{-22}$ M) and $(CN)_2(10^{-16}$ M) are low enough to omitted them; thirdly, the value of pH simulated by 26 differential equations is not lower than 9, so it is reasonable that the reactions of pH<7 are not included in the primary mechanism to elucidate the oscillation.

Interaction of PUT with the oscillating system

PUT can scavenge the active-oxygen free radicals such as HO_2·, HO· and O_2·–directly [20]. In this oscillating system, the active oxygen free radicals exist primarily in HO_2· and the concentration of HO·($\approx10^{-22}$ M by calculation) is rather low. When HO_2· reacts with PUT, the concentration of HO_2· was decreased sequentially. As a result, $^-$OS(O)CN, generated autocatalytically in (R14) of the positive feedback loop, will not be consumed as quickly as in the absence of PUT. Consequently, the accumulation of –OS(O)CN will simultaneously accompany the

increasing yield of Cu^{2+}, which will further cause the more appearance of HO_2–Cu(I). Therefore, PUT added into the system can delay the negative feedback loop and prolong the survival of the yellow superoxide-copper(I) complex, thus increase the oscillation period as observed in the experiments.

The mechanism that how PUT cleans up the active-oxygen free radicals directly has not reported. We suppose that PUT could react with the active-oxygen free radicals to produce other less active free radical through a quick equilibrium, which will cause the decrease of active-oxygen free radicals in every moment than before.

$$PUT+HO_2· \overset{k_{19}}{\leftrightarrow} product1· \qquad (R19)$$

$$PUT+HO· \leftrightarrow product2· \qquad (R20)$$
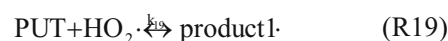
where product1· and product2· express the products which have lower reaction activities. According to our calculation, the concentration of HO· is less than approximate 10^{-22} M, so (R20) is not taken into account.

Numerical simulation

Simulation on the oscillating system by the simulated mechanisms

All reactants and intermediates, 16 in total, that appear on the left-hand side of (R1)–(R18), are taken as independent variables. For simplicity, the SCN^-'s and OH^-'s in braces are not included in the stoichiometry, which are dummy symbols here to show the sense of the chemistry. In simulation, the initial concentrations of KSCN, H_2O_2, $CuSO_4$ and NaOH are 0.025, 0.204, $1.0·10^{-4}$, 0.0257 M. The initial concentrations of the intermediates are assigned zero. For making the calculated results consistent with the experimental observations as much as possible, the values of f, k_{10} and k_{11} are assigned 0.40, $1.0·10^{-3}$ and $4·10^{-1}$. The

Table 2 Rate constants in the mechanism for H_2O_2–KSCN–Cu(II)

Constant	Value	Constant	Value/
k_1	$4.0·10^5$ M^{-2} s^{-1}	k_2	k_1/Kapp[a]
k_3	$4.0·10^{-2}$ s^{-1}	k_4	80 M^{-1} s^{-1}
k_5	$3.0·10^{-3}$ M^{-1} s^{-1}	k_6	1.2 M^{-1} s^{-1}
k_7	$2.0·10^3$ M^{-1} s^{-1}	k_8	$4.0·10^3$ M^{-1} s^{-1}
k_9	4.0 M^{-1} s^{-1}	k_{10}	variable param.
k_{11}	variable param.	k_{12}	$1.2·10^4$ M^{-1} s^{-1}
k_{13}	$8.0·10^6$ M^{-1} s^{-1}	k_{14}	$4.0·10^5$ M^{-1} s^{-1}
k_{15}	$8.0·10^3$ M^{-1} s^{-1}	k_{16}	$6.0·10^5$ M^{-1} s^{-1}
k_{17}	$4.0·10^8$ M^{-1} s^{-1}	k_{18}	0.8 M^{-1} s^{-1}

[a]Kapp=$(4.0+9.6·10^2·[OH^-])/(4.608·10^{13}·[OH^-]^4+$
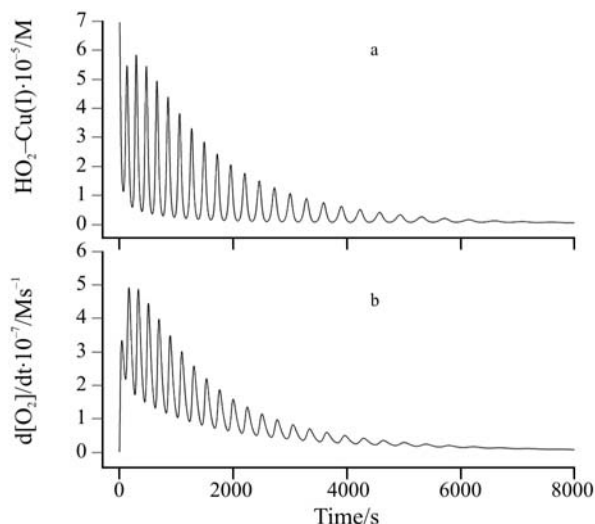$+1.32·10^{11}·[OH^-]^3)$ as indicated in [19]

Fig. 8 Calculated bath oscillations in a – HO_2–Cu(I) and b – $d[O_2]/dt$ curves. The initial concentrations are: [KSCN], 0.025 M; [H_2O_2], 0.204 M; [CuSO$_4$], $1.0 \cdot 10^{-4}$ M; [NaOH], 0.0257 M. f=0.40

values of rate constants are listed in Table 2 from [16] and are slightly adjusted for our experimental temperature is higher than theirs. With computational effort of the 16 differential equations by the method of Gear [21], we obtain the stimulated results in agreement with the experimental findings, such as the periodical oscillation of HO_2–Cu(i), $d[O_2]/dt$ (Fig. 8). In the same conditions as Fig. 1, the oscillating period calculated is 178 s and the numbers of oscillation are about twenty, which approximates the experimental observations. In addition, it can be seen that the oscillations appear in the form of damping from Fig. 8.

Simulation the effect of PUT on the oscillating system

When PUT was added into the reaction system, the (R19) was taken into account in the mechanism. K_{19} is the equilibrium constant of (R19).

$$K_{19} = \frac{[\text{product1} \cdot]}{[\text{PUT}][\text{HO}_2 \cdot]}$$

where [product 1·]=[HO_2·]$_0$–[HO_2·]
 Then it can be attained:

$$[\text{HO}_2 \cdot] = \frac{[\text{HO}_2 \cdot]_0}{1 + K_{19}[\text{PUT}]}$$

where [HO_2·]$_0$ and [HO_2·] are the concentrations in the absence and presence of PUT, respectively. In the calculation, the value of K_{19} is assigned for

$1 \cdot 10^4$ mol^{-1} L and the differential equation of $d[HO_2 \cdot]/dt$ is described as follows:

$$d[\text{HO}_2 \cdot]/dt = (k_3[\text{HO}_2 - \text{Cu(I)}] - 2k_4[\text{HO}_2 \cdot]^2 - k_{14}[^-\text{OS(O)CN}][\text{HO}_2 \cdot])/(1 + k_{19}[\text{PUT}])$$

Figure 9 gives the profile of [HO_2·] *vs.* time (s) in the absence and presence of PUT. It is very obvious that the oscillating period increases with the increase of PUT. The oscillating numbers decrease with that. Figure 10 gives the relation between t_p and PUT concentration, namely: t_p=178.4+35.58[PUT], (R=0.9997). This is in good agreement with the experimental findings (Table 3).
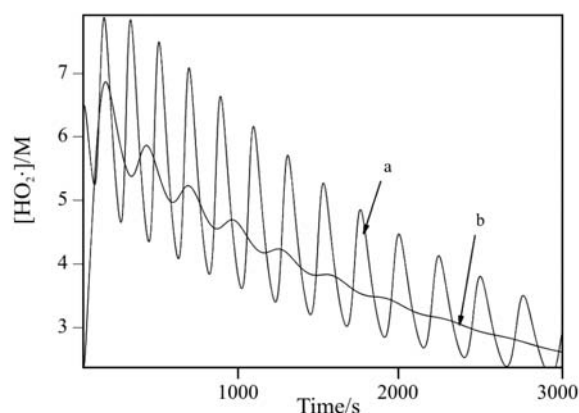

Fig. 9 The calculated concentration of HO_2· *vs.* time (s) in a–[PUT]=0.0 M and b–[PUT]=2.26·10^{-4} M. The initial concentrations are: [KSCN], 0.025 M; [H_2O_2], 0.204 M; [NaOH], 0.0257 M; [CuSO$_4$], 1.00·10^{-4} M (303.15 K)
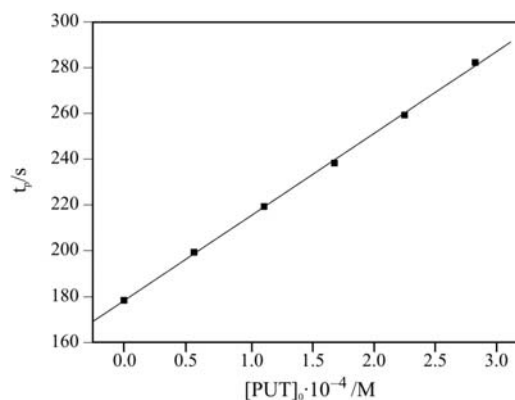

Fig. 10 Calculated oscillating period (t_p) *vs.* the concentration of PUT: The initial concentrations are: [KSCN]$_0$, 0.025 M; [H_2O_2], 0.204 M; [NaOH], 0.0257 M; [CuSO$_4$], 1.00·10^{-4} M (303.15 K)

Table 3 The oscillating period of experiment (exp.) and calculation (cal.) in different concentrations of PUT

[PUT]/M	0.0	5.65·10^{-5}	1.13·10^{-4}	1.70·10^{-4}	2.26·10^{-4}	2.83·10^{-4}
t_p/s (exp.)	158	176	205	222	241	–
t_p/s (cal.)	178	199	219	238	259	282

Conclusions

The calorimetric method has been used to investigate H_2O_2–KSCN–$CuSO_4$–NaOH oscillating system. The system was optimized by changing each reactant while keeping all other constants, and our work shows that:

$$t_p \propto [KSCN]\ln(1/[H_2O_2])[CuSO_4]^{-1} \cdot$$
$$\cdot f[NaOH]\exp(45.85/RT)$$

Furthermore, the effect of PUT on this system was investigated. A linear relationship between the oscillating period and the concentration of PUT is obtained, $t_p \propto [PUT]$. This is probably attributable to a quick equilibrium, which exists between $HO_2\cdot$ and PUT.

A simplified mechanism for the H_2O_2–KSCN–$CuSO_4$ system, including 18 kinetic steps and 16 variables, is put forward, which has shown great success in simulating the observed oscillations in the closed condition. And the calculated results account well for most of the major dynamical features.

In addition, by the numerical simulation about the behavior of PUT on the oscillating system, the calculated results are in good agreement with our experimental findings and accordingly prove our equilibrium supposition reasonable. Besides this supposition, we also tempt to put forward another supposition, a reaction supposition, namely, PUT reacts with $HO_2\cdot$ to reduce the concentration of $HO_2\cdot$. But the calculated results show nearly no change of t_p and the number of oscillation occur, which give a denial to the reaction supposition. But the genuine mechanism that putrescine is a scavenger of activity-oxygen free radicals has not been elucidated. Whether it can scavenge $HO_2\cdot$ though a quick equilibrium requires further investigation.

In deed, where is a reaction, there is an output of heat. Calorimetric method can be used for studying almost all of reaction system, so long as the heat is apt to be able to be measured. Furthermore, calorimetry has the advantages of being unspecific, non-invasion and insensitive to the electrochemical and optical properties of the investigated system, so it is also a very useful measure to study the oscillating system.

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