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Combined capillary electrophoresis and high performance liquid chromatography studies on the kinetics and mechanism of the hydrogen peroxide–thiocyanate reaction in a weakly alkaline solution

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ABSTRACT

The hydrogen peroxide–thiocyanate reaction has been reinvestigated by means of capillary electrophoresis and high performance liquid chromatography under weakly alkaline conditions at 25.0 ± 0.1 °C. Concentration–time series of thiocyanate, sulfate and cyanate have been followed by capillary electrophoresis as well as that of thiocyanate and hydrogen peroxide by HPLC. It has been clearly demonstrated that O_xSCN^- (where $x=1, 2$ and 3) cannot be accumulated in detectable amount in contrast to the results of Christy and Egeberg, hence these species can only be regarded as short-lived intermediates. It has been shown that the overall rate law is first-order with respect to both reactants, but no pH-dependence was observed within the pH range of 8.86–10.08. A simple kinetic model has been proposed to fit all the concentration–time curves simultaneously at five different pHs demonstrating the powerful combination of the experimental techniques CE and HPLC with simultaneous evaluation of kinetic curves. It is also enlightened that the quality of the buffer strongly affects the rate of the overall reaction that increases in the order of application of ammonia, phosphate, carbonate and borate, respectively at a constant ionic strength and pH.

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1. Introduction

Oxidation of thiocyanate (SCN^-) has received considerable attention in the past due to its possible use of quantitative determination of thiocyanates [1–6] as well as that of potential industrial applications [7]. One of the most thoroughly studied oxidation of thiocyanate is its reaction with hydrogen peroxide. The first comprehensive research showed that this reaction is essentially pH-independent [1] in between pH 4.0 and 12.0, but at higher acidity an acid-catalyzed pathway also appears [8]. Based on iodometric titrations it was assumed that the rate determining step of the oxidation is a formal oxygen transfer from hydrogen peroxide to the thiocyanate molecule to give hypothiocyanite. Further oxidation or disproportionation of this species essentially leads to the formation of sulfate, cyanate, bicarbonate, ammonia, cyanide and sulfite depending on the initial concentration ratio of the reactants. More recently a capillary electrophoresis study was published intending to use the benefit in recent development of experimental techniques to elucidate the kinetics and mechanism of this reaction in nearly neutral solutions [9]. Several new conclusions have been drawn that contradicted to earlier results. Among them the most surprising statement was that $OSCN^-$ was identified as a long-lived intermediate in the electropherograms hence it was concluded that the rate determining step of the reaction is further reaction of hypothiocyanite with hydrogen peroxide. This result looks quite ambiguous in view of the fact that hypothiocyanite can only be produced in the presence of huge excess of thiocyanate from its oxidation by hypohalites [10]. Recent advances [11,12] in the $OSCN^-$ chemistry also suggest that in nearly neutral solution the half-life of this species is approximately 20 s, hence a peak with a migration time longer than 4 min measured by capillary electrophoresis cannot be attributed to this species.

Our aim is here therefore to reinvestigate the thiocyanate–hydrogen peroxide reaction by combined CE and HPLC techniques with the help of tracking concentration–time curves of as many species as possible and employing a kinetic model with simultaneous evaluation of the kinetic curves.

2. Experimental section

Materials. Analytical or higher grade reagents, without further purification, were used in these experiments, including potassium

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thiocyanate, potassium nitrate, potassium sulfate, lithium hydroxide, potassium cyanate, hexadimethrine bromide (HDB), tetraethylammonium hydroxide (TEAOH) and borax. Hydrogen peroxide (30% solution) was purchased from Sigma–Aldrich. Heavy metal, sulfate, phosphate and chloride impurities of the concentrated hydrogen peroxide solution were assured to be less than 0.0003%. Additional stabilizers of the stock solution were excluded. Stock solutions were protected from light and were standardized by $KMnO_4$ titration once a week. Hypothiocyanite was prepared by hydrolysis of thiocyanogen at pH 13 as described in the literature and was used immediately due to its instability [10]. The fresh hypothiocyanite solution was qualitatively tested by UV/vis spectrometer (PerkinElmer Lambda 40) at the $\lambda_{max} = 376$ nm. All solutions were prepared with distilled water ($18.2\ M\Omega^{-1}\ cm^{-1}$) from a Milli-Q purification system. pH was mainly controlled by borate–saline buffer between 8.86 and 10.08, but some control experiments in the presence of ammonia, phosphate and carbonate buffers were also investigated. The total concentration of buffer components was always kept constant at 0.1 M.

Instruments and methods. The reactions were followed by CE and HPLC instruments simultaneously. CE analysis was carried out on a Beckman Coulter P/ACE MDQ capillary electrophoresis system equipped with a photodiode array detector. A fused silica capillary of 57.5 cm (75 μm i.d. × 375 μm o.d.) was used. The condition of the kinetic runs was as follows: separation voltage 15 kV, capillary temperature 25 °C, cathodic pressure injection for 5 s with 0.5 psi. An indirect ultraviolet method was employed, using a 20 mM KNO_3 (as an absorbing co-ion to elevate the baseline) and 2.0×10^{-5} mM HDB solution adjusted to certain pH with LiOH as background electrolyte. Two detection wavelengths were selected at 210 and 225 nm s for qualitative and quantitative analyses of different species. The HPLC separation was conducted on an Agilent 1100 system, which includes a G1379A degasser, a G1311A quaternary pump, a G1316 column thermostat and a G1315A multiple wavelength detector. A Phenomenex Gemini C_{18} silicon column (5 μm, 250 × 4.6 mm i.d.) was used. The mobile phase consisted of 20 mM TEAOH as ion-pair agent and methanol in a volumetric ratio of 95:5. To shorten the time of analysis the flow rate was set to be 1.0 cm^3/min The pH of background electrolyte, mobile phase and reaction solution was all kept at the same value to prevent the possible change either in the rate of reaction or in the mechanism due to a pH jump.

Reaction was initiated by introducing appropriate quantities of H_2O_2 and KSCN into the buffer solutions. A sample was withdrawn from the reaction mixture and analyzed with CE and HPLC at regular intervals while the reaction was kept at constant temperature with continuous stirring after initiation. Reaction solution and background electrolyte were treated with 0.45 μm millipore filter before introduced to CE and HPLC. Several series of experiments were carried out in the concentration range of 2.0–14.0 mM and 5.0–40.0 mM in the case of thiocyanate and hydrogen peroxide, respectively at five different pHs.

Data treatment. Electrophoretic data at 210 nm (for CE) and chromatographic data 230 nm (for HPLC) were used for most of the kinetic experiments. Calibration curves for thiocyanate, sulfate, cyanate ions and hydrogen peroxide were determined to convert the measured peak areas into concentrations. The correlation coefficients were always found above 0.999 indicating a perfect linear relationship between the peak area and the concentration. Altogether 185 concentration–time kinetic curves (including $[SCN^-]$–time measured with both CE and HPLC, $[SO_4^{2-}]$–time, $[OCN^-]$–time and $[H_2O_2]$–time) were used for simultaneous data evaluation. To obtain the kinetic parameters for the proposed model the ZiTa program package was used [13].

3. Results

3.1. Component separation and detection

With an optimization of separation conditions, sample analysis was completed and was found to be well-separated within 4.3 min for CE and within 5.3 min for HPLC experiments. This process does not influence the mechanism due to the significantly longer reaction time compared to separation time. With an indirect ultraviolet method in CE analysis, SCN^-, SO_4^{2-} and OCN^- can be detected. SCN^- displays a negative electrophoretic peak at 210 nm and a positive peak at 230 nm due to its relatively lower and higher absorption compared to baseline, respectively. Besides migration time, this feature is also used for the qualitative test of SCN^- in CE. Sulfate lacking suitable chromophores can also be measured with a negative peak at both wavelengths. Because hydrogen peroxide cannot be detected with CE, its concentration was determined by HPLC. The conditions, where H_2O_2 was detected, were also suitable for determining the concentration of thiocyanate ion by HPLC. It also provided us a good opportunity to compare the $[SCN^-]$–time series measured by both methods. The agreement of these data within the experimental error (see later) convinced us that these methods can be used for simultaneous evaluation of the kinetic curves.

Fig. 1 indicates typical electropherograms detected by CE during a single kinetic run. As seen under these experimental conditions sulfate has the smallest migration time (t=3.53 min). The second peak in the electropherograms (t=3.63 min) belongs to thiocyanate allowing us to follow its concentration as a function of time as well. It is also clear that two additional peaks also appear in the electropherograms having migration times as 3.75 and 4.22 min. Having known that Christy and Egeberg [9] assumed that a migration peak after thiocyanate may be attributed to hypothiocyanite we first sought a direct experimental evidence of this fact injecting freshly prepared $OSCN^-$ solution to CE meanwhile measuring simultaneously its UV/vis absorption. This experiment proves that no peak appears at 3.75 min migration time, while the characteristic absorption band of $OSCN^-$ around 376 nm can be easily seen in the spectroscopic measurement. From this we concluded that Christy and Egeberg erroneously

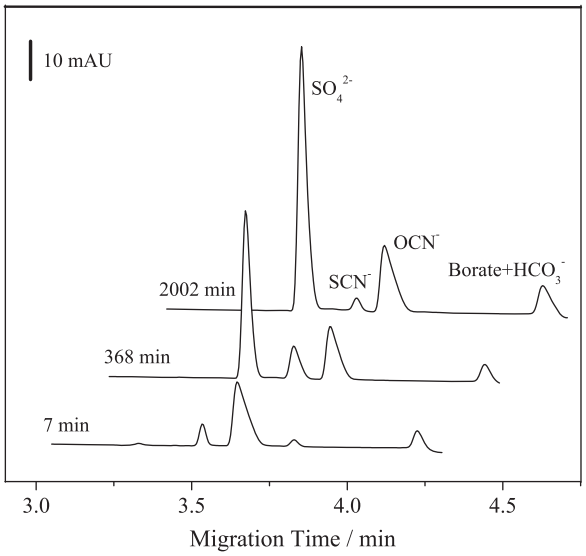

Fig. 1. Typical CE electropherogram taken at different time points during the course of the reaction. All peaks are going up in the negative direction. For better visibility electropherograms are shifted both horizontally and vertically by 0.15 min and 18 mAU, respectively. Conditions: $[SCN^-]_0$=5.0 mM; $[H_2O_2]_0$=20.0 mM; pH 9.53; detection wavelength is 210 nm.

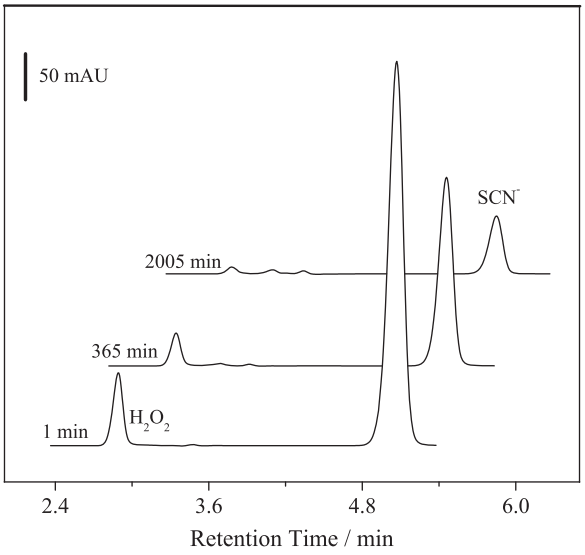

Fig. 2. Typical HPLC chromatogram taken at different time points during the course of the reaction. For better visibility chromatograms are shifted both horizontally and vertically by 0.45 min and 85 mAU, respectively. Conditions: $[SCN^-]_0$= 5.0 mM; $[H_2O_2]_0$=20.0 mM; pH 9.53; detection wavelength is 230 nm.

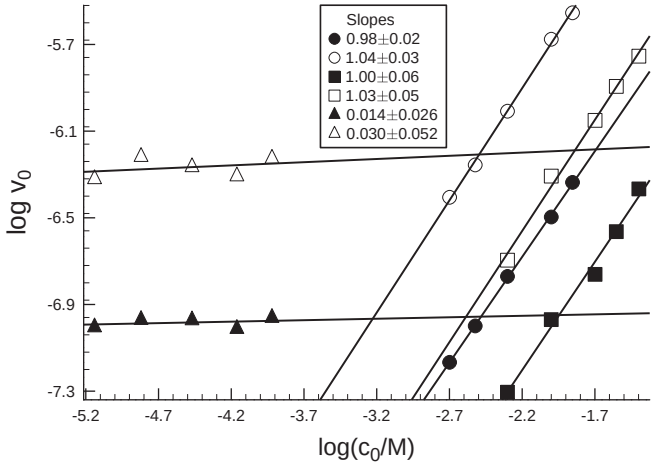

Fig. 3. Initial rate studies. v_0 is defined as $d[SCN^-]/dt$ (filled symbols) and $d[H_2O_2]/dt$ (empty symbols) at t=0 s. Conditions are as follows: (●,○) pH 9.84, $[H_2O_2]_0$=20.0 mM; (■,□) pH 9.18; $[SCN^-]_0$ =5.0 mM; (▲,△) $[SCN^-]_0$=5.0 mM; $[H_2O_2]_0$=10.0 mM. c_0 corresponds to the concentration of the given species to be changed during a series of run meanwhile keeping all the other concentrations constant.

assigned this migration peak to $OSCN^-$. Further elucidation of the migration peaks (addition of standard solution to the reaction mixture) revealed that the first peak belongs to OCN^- and the second peak can be assigned to bicarbonate and buffer components. Therefore we suggest that in fact Christy and Egeberg found the peak of OCN^- in their measurements rather than that of $OSCN^-$.

Fig. 2 depicts typical chromatograms measured by HPLC. The peaks at 2.89 and 5.07 min represent hydrogen peroxide and thiocyanate ion, respectively. Their peak areas can also be converted into concentration meaning that with simultaneous detection of CE and HPLC the concentrations of both reactants and that of several end-products can be determined.

3.2. Initial rate studies

Wilson and Harris have found a simple rate equation to be valid between the pH range 4.0 and 12.0 for the thiocyanate–hydrogen peroxide reaction [1]:

$$-\frac{d[SCN^-]}{dt} = k_w[SCN^-][H_2O_2], \quad (1)$$

where k_w was found to be $0.031 \pm 0.003\ M^{-1}\ min^{-1}$ by iodometric titration. The extended pH range using acetate and phosphate buffers already suggests that formal kinetic order of the reactants seems to be independent of the quality of buffer. In contrast with the conclusion drawn by Wilson and Harris the formal kinetic order of thiocyanate is zero in the presence of phosphate buffer according to Christy and Egeberg's report [9], while that of hydrogen peroxide is one by using the isolating kinetic method. Hence it was concluded that the following rate equation should be valid [9]

$$-\frac{d[SCN^-]}{dt} = k_c[H_2O_2] \quad (2)$$

where $k_c=(9.6 \pm 0.1) \times 10^{-5}\ min^{-1}$. Though it is also true that they also evaluated their kinetic data by the method of initial rate studies. Surprisingly, it showed a formal kinetic order of unity with respect to thiocyanate and they found $k_w=0.039 \pm 0.002\ M^{-1}\ min^{-1}$ to be in quite a good agreement with Wilson and Harris's report. In spite of this good agreement Christy and Egeberg still claimed according to their data that the reaction is zero order with respect to thiocyanate, possibly because it was believed that initial rate studies did not give precise information about the formal kinetic order of the reactant due to unknown extent of the reaction studied by Wilson and Harris.

We therefore decided to determine the formal kinetic order of the reactants from our data as well. Fig. 3 indicates the results of the initial rate studies clearly confirming Wilson and Harris result's on obtaining the formal kinetic orders of both reactants to be one as well as that of hydroxide ion to be zero meaning that the reaction is essentially independent of pH within the range studied. Although the majority of our measurements has been performed in the presence of borate buffer we have also checked the questionable kinetic order of thiocyanate in the presence of phosphate buffer. As seen in Supplementary Material we clearly confirmed Wilson and Harris's results about obtaining a formal kinetic order of thiocyanate to be unity. Consequently it seems to be well-established that the formal kinetic orders of the reactants are independent of the quality of buffer used in the experiments. We shall see later that this statement is not only valid in the case of acetate, phosphate and borate buffer but also in that of ammonia and carbonate. A key question however still remains, how Christy and Egeberg's data can indicate such a seemingly unambiguous zero order with respect to thiocyanate. Inspecting their figures (p. 1055 of the given article) suggest that even at relatively high conversion (80% of initially added thiocyanate reacted) a linear relationship was found in the relative concentration–time curves. As we shall see later such a decay of $[SCN^-]$ was never observed in any of our measurements and was not reported in any previous studies [1,2]. Therefore we suggest that the difference might arise from either the different experimental conditions used (but it is difficult to understand how such basically different ones can be obtained) or there might be a hidden artifact during separation or detection resulting in an erroneous conclusion.

3.3. Stoichiometry and important characteristics of the measured kinetic curves

In agreement with Wilson and Harris's study [1] we strengthened the fact that all oxidized sulfurs appeared in the form of sulfate. Furthermore OCN^- is an end-product in the pH range of

Table 1
Fitted rate coefficients of the proposed kinetic model.

Step	Rate equation	Parameter value
$SCN^- + 4H_2O_2 \rightarrow$ $SO_4^{2-} + OCN^- + 3H_2O + 2H^+$	$k_1[SCN^-][H_2O_2]$	$(2.91 \pm 0.03) \times 10^{-3}\ M^{-1}\ s^{-1}$
$2H_2O_2 \rightarrow 2H_2O + O_2$	$k_2[H_2O_2]$	$(9.84 \pm 0.53) \times 10^{-7}\ s^{-1}$
$OCN^- + 2H_2O \rightarrow HCO_3^- + NH_3$	$k_3[OCN^-]$	$(7.13 \pm 0.52) \times 10^{-7}\ s^{-1}$

8.86–10.08 at our time ranges, although a slight increase in its concentration was also observed in agreement with previous studies [1,14]. The measured $[SCN^-]$–time and $[H_2O_2]$–time kinetic curves suggest that the consumed hydrogen peroxide thiocyanate ratio is 4:1, i.e., the stoichiometry of the reaction can be established as

$$SCN^- + 4H_2O_2 \longrightarrow SO_4^{2-} + OCN^- + 2H_2O + 2H^+ \quad (3)$$

Wilson and Harris [1] also reported that OCN^- is not a stable end-product and can be decomposed into ammonia and hydrogen carbonate ions [14]:

$$OCN^- + 2H_2O \longrightarrow NH_3 + HCO_3^- \quad (4)$$

As we shall see in some cases concentration of OCN^- also decreased slightly in our experiments meaning that Eq. (4) may also play a minor role in describing the kinetics of the title reaction.

It should also be noticed that in excess of hydrogen peroxide, a slow but steady decay can be observed in the concentration of hydrogen peroxide meanwhile the concentration of the end-products remains the same within the experimental error. It clearly means that catalytic or spontaneous decomposition of hydrogen peroxide should also be considered in describing the kinetic curves simultaneously.

3.4. Proposed kinetic model

As a start to fit our kinetic data we started the evaluation procedure with simply considering the stoichiometric equation (3) with having a rate equation first order with respect to both reactants supplemented with first order decomposition of hydrogen peroxide as well as that of cyanate ion. We found that these three equations can describe our data pretty well. Altogether more than 4800 concentration–time data pairs were evaluated simultaneously. The average deviation was found to be 4.9%, which we believe is close to the experimentally achievable limit of error. Table 1 contains the kinetic parameters of the fit. Figs. 4–6 depict that the proposed kinetic model is working properly under our experimental conditions.

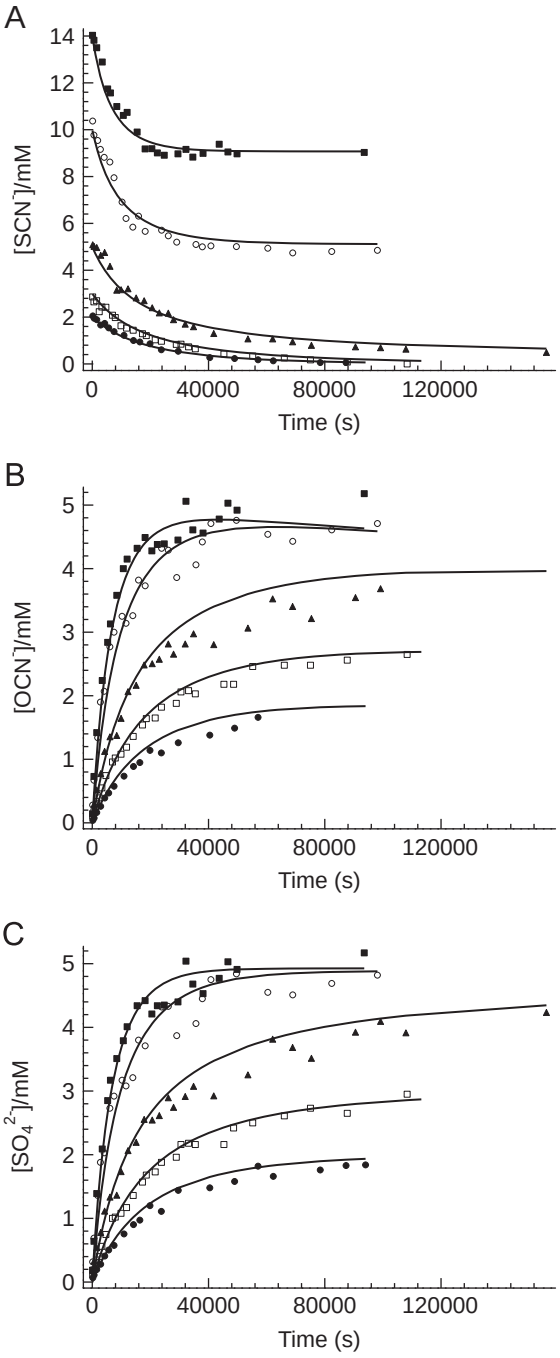

Fig. 4. Measured (symbols) and calculated (solid lines) concentration–time series of thiocyanate (A), cyanate (B) and sulfate (C) ions in the presence of borate buffer at pH 9.18 and at $[H_2O_2]_0$=20.0 mM. The measured curves were obtained by CE. $[SCN^-]_0$/mM=2.0 (•); 3.0 (□); 5.0 (▲); 10.0 (○); 14.0 (■).

4. Discussion

Specific rate constant $k_w = 0.031\ M^{-1}\ min^{-1}$ and $0.039\ M^{-1}\ min^{-1}$ of the reaction determined by Wilson and Harris [1] and by Christy and Egeberg [9], respectively can be transformed into SI unit as $k_w = 5.17 \times 10^{-4}\ M^{-1}\ s^{-1}$ or $6.5 \times 10^{-4}\ M^{-1}\ s^{-1}$. Comparing these values to our k_1 parameter indicates a circa four–six times difference that possibly stems from applying borate buffer in our case. As it was already noticed by Wilson and Harris [1] borate increases the rate of consumption of hydrogen peroxide hence the rate coefficient as well. We sought a direct experimental evidence for this effect with changing the quality of buffer meanwhile keeping the ionic strength and pH constant. The results can be seen in Fig. 7.

It is clear that the quality of the buffer affects the value of k_1. As indicated in Table 2 the slowest rate can be measured in the case of ammonia buffer $k_1 = 3.34 \times 10^{-4}\ M^{-1}\ s^{-1}$. In presence of carbonate buffer we determined a somewhat higher value ($1.28 \times 10^{-3}\ M^{-1}\ s^{-1}$) for k_1, while the largest rate coefficient ($k_1 = 2.91 \times 10^{-3}\ M^{-1}\ s^{-1}$) was found in the presence of borate buffer. Although complete elucidation of the effect of borate is out of the scope of this study it is probably due to the specific formation of peroxoborate species [15]. Nevertheless these results explain why our k_1 value differs from the values determined by previous studies. Christy and Egeberg [9] used phosphate buffer while Wilson and Harris [1] used mixture of ammonia,

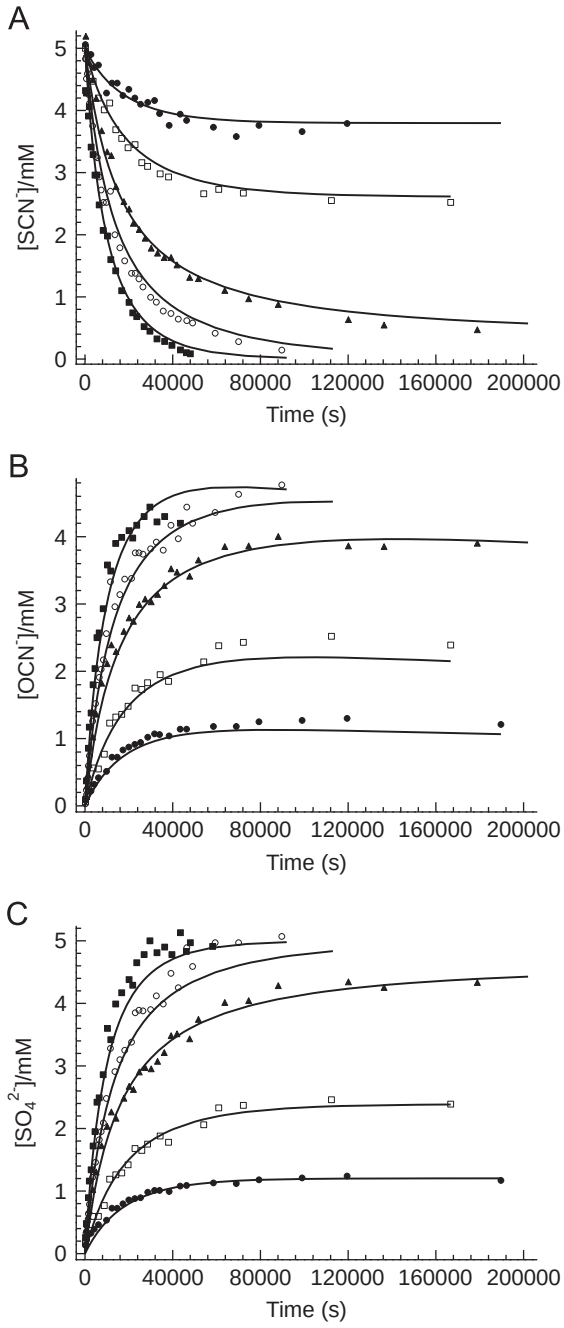

Fig. 5. Measured (symbols) and calculated (solid lines) concentration–time series of thiocyanate (A), cyanate (B) and sulfate (C) ions in the presence of borate buffer at pH 9.53 and at $[SCN^-]_0$=5.0 mM. The measured curves were obtained by CE. $[H_2O_2]_0$/mM=5.0 (●); 10.0 (□); 20.0 (▲); 28.0 (○); 40.0 (■).

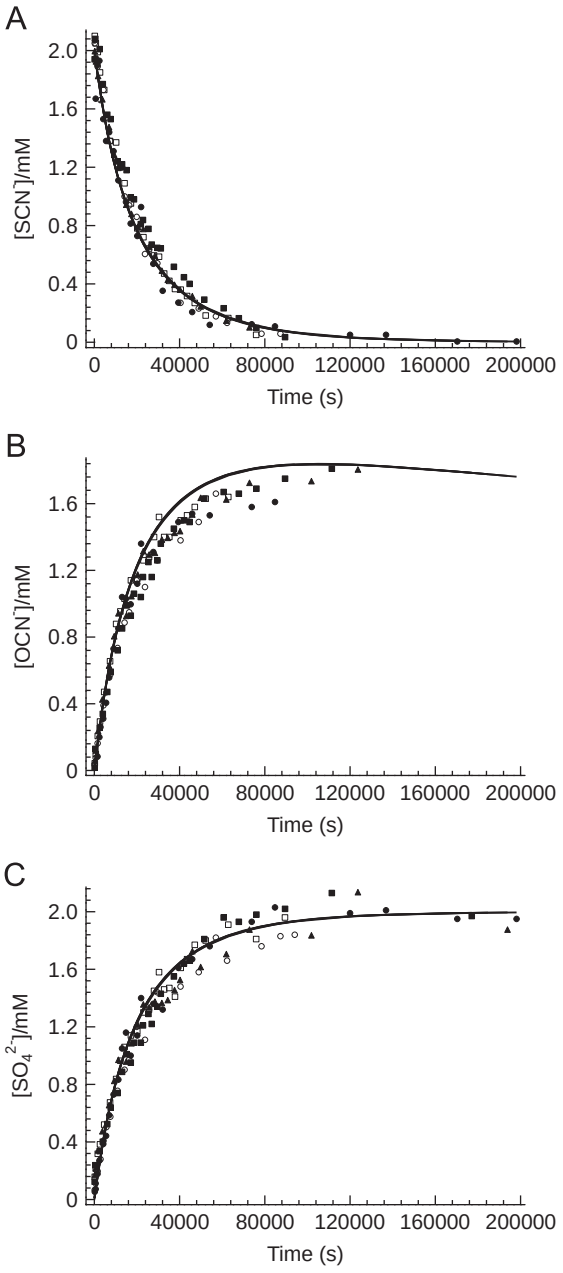

Fig. 6. Measured (symbols) and calculated (solid lines) concentration–time series of thiocyanate (A), cyanate (B) and sulfate (C) ions in the presence of borate buffer at $[H_2O_2]_0$=20.0 mM and at $[SCN^-]_0$=2.0 mM. The measured curves were obtained by CE. pH 10.08 (●); 9.84 (□); 9.53 (▲); 9.18 (○); 8.86 (■).

phosphate and acetate buffers in their experiments. In view of our results it is also easily understood why Wilson and Harris determined a slightly lower value than Christy and Egeberg did, because it is simply due to the application of ammonia that results in the slowest reaction rate.

Another interesting phenomenon caused by different buffers should also be mentioned. As seen our experiments indicate that in the case of borate and ammonia buffers there is no difference in the rate constant of the spontaneous (or catalytic) decomposition of hydrogen peroxide within the experimental error (see Table 2) therefore regardless of the buffer it seems that decomposition of hydrogen peroxide cannot be avoided under our experimental conditions. In contrast to that, however, in the case of carbonate buffer more than an order of magnitude higher decomposition rate of hydrogen peroxide could be determined. In addition to that a relatively huge shift can also be observed in the consumed hydrogen peroxide thiocyanate ratio in the presence of carbonate buffer. Fig. 7 suggests that this ratio may increase to approximately 7. On the one hand these experimental facts may easily be explained by a trace amount of transition metal impurities to be presented in the carbonate stock solutions. The effect of these impurities is already well-known and realized by several independent research groups [16–18] studying the stability of hydrogen peroxide in the presence of carbonate ion. As one may notice under our experimental conditions rate coefficient k_2 is approximately an order magnitude lower than the one reported by Lee et al. [18] at slightly elevated temperature 40 °C and at a different ionic strength. On the other hand

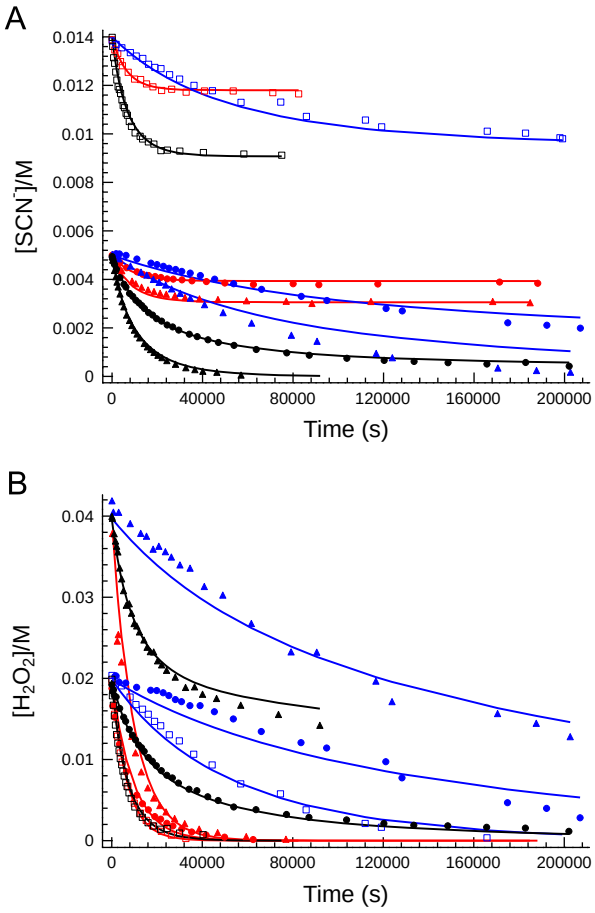

Fig. 7. Effect of application of different buffers at pH 9.53 and at constant buffer components concentration (0.1 M) on the concentration–time series of thiocyanate (A) and that of hydrogen peroxide (B). The kinetic curves were measured by HPLC. Black, blue and red symbols and solid lines correspond to different buffers such as borate, ammonia and carbonate, respectively. Initial concentrations are as follows (independent of the color): (●) $[H_2O_2]_0$=20.0 mM and $[SCN^-]_0$=5.0 mM; (□) $[H_2O_2]_0$=20.0 mM and $[SCN^-]_0$=14.0 mM; (▲) $[SCN^-]_0$=5.0 mM; $[H_2O_2]_0$=40.0 mM. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

Table 2
Comparison of rate coefficients in the presence of different buffers.

Step	Ammonia	Phosphate	Carbonate	Borate
$k_1 \times 10^4\ M^{-1}\ s^{-1}$	3.34	5.2 (Ref. [1]) 6.5 (Ref. [9]) 3.6 (This work)	12.8	29.1
$k_2 \times 10^7\ s^{-1}$	10.0	N/A	417	9.84

formation of peroxymonocarbonate ion from the hydrogen peroxide–bicarbonate reaction may also have a reasonable impact on the stoichiometry of the thiocyanate–hydrogen peroxide reaction [19].

Our results clearly demonstrated that other species than cyanate ion and sulfate cannot be detected under our experimental conditions hence all species like $OSCN^-$, O_2SCN^- and O_3SCN^- can only be short-lived intermediates. It means that it is *impossible* to derive the mechanism of the title reaction only a plausible sequence of reactions can be proposed with a rate-determining initiating step. It is also out of question that borate buffer has a significant catalytic effect on the kinetics of the reaction and carbonate buffer also has a series impact especially on the stoichiometry of the reaction. We suggest therefore only a reasonable possibility (see later) but it should be emphasized that any other sequence of reaction leading to the given stoichiometry would equally describe our kinetic data. We would like to emphasize again that applying constant buffer concentrations do not provide solid bases to assign unambiguously the catalytic effect of buffer components to any of the plausible reactions of the sequence indicated below. Encountering, however, that hydrogen peroxide reacts with bicarbonate and borate to form peroxymonocarbonate and monoperoxoborate and/or diperoxoborate, respectively in a rapid equilibrium and these species are also capable of oxidizing thiocyanate. The overall effect is that the rate coefficient of the rate determining step is affected by the concentration of buffer components. In other words k_1 has to be a function of buffer concentration but exact dependencies cannot be drawn in lack of such investigations where the concentration of borate, carbonate, phosphate and ammonia was varied. Considering these facts a plausible sequence of reaction may be outlined as follows:

$$SCN^- + H_2O_2 \xrightarrow{k_5,\ \text{r.d. step}} OSCN^- + H_2O \quad (5)$$

$$OSCN^- + H_2O_2 \xrightarrow{k_6,\ \text{fast}} O_2SCN^- + H_2O \quad (6)$$

$$O_2SCN^- + H_2O_2 \xrightarrow{k_7,\ \text{fast}} O_3SCN^- + H_2O \quad (7)$$

$$O_3SCN^- + H_2O_2 \xrightarrow{k_8,\ \text{fast}} SO_4^{2-} + OCN^- + 2H^+ \quad (8)$$

where the value of k_5 equals to that of k_1 and for rest of the rate coefficients only a lower limit of $10\ M^{-1}\ s^{-1}$ can be obtained. An alternative possibility may also be taken into consideration, i.e., replacement of Eqs. (6) and (7) with the following reactions:

$$2OSCN^- \xrightarrow{k_9,\ \text{fast}} O_2SCN^- + SCN^- \quad (9)$$

$$2O_2SCN^- \xrightarrow{k_{10},\ \text{fast}} O_3SCN^- + OSCN^- \quad (10)$$

It should be mentioned that in acidic solution, as an analogy of this pathway, the second-order decomposition of hypothiocyanous acid as well as that of cyanosulfurous acid accounts for description of the kinetic curves in the title reaction studied by Figlar and Stanbury [20]. We have examined this opportunity and found if these processes are fast enough (k_9 and $k_{10} > 10^6\ M^{-1}\ s^{-1}$) our kinetic data can be equally well described because the necessary requirement for $OSCN^-$, O_2SCN^- and O_3SCN^- to be short-lived intermediates is fulfilled. The only difference is that in the latter case the value of $k_5 = 3 \times k_1$ could be determined. The reason can be easily understood: sequence of Eqs. (5)–(7) displays three times higher rate for consumption of hydrogen peroxide than that of Eqs. (5), (9) and (10) meaning that three times higher rate coefficient is needed for the rate determining step (Eq. (5)) to achieve the same results.

One important issue should also be mentioned namely that neither of these sequences is able to explain the shift of the stoichiometric ratio of the reaction from 4 to 3 in acidic solution. We suggest that it is worth considering that for decay of O_3SCN^- Eq. (8) is not the only possibility. If at acidic condition hydrolysis [20] of O_3SCN^- can compete with Eq. (8) in a pH-dependent reaction

$$O_3SCN^- + H_2O \longrightarrow SO_4^{2-} + HCN + H^+ \quad (11)$$

then it easily explains why no cyanide ion appears around neutral and alkaline conditions in contrast to acidic conditions where hydrogen cyanide is exclusively found [1].

5. Conclusion

In this work reinvestigation of the kinetics of the hydrogen peroxide–thiocyanate reaction was carried out due to a questionable result reported recently by Christy and Egeberg [9] that contradicted to our recent knowledge on the chemistry of hypothiocyanite ion. Concentrations of different species such as hydrogen peroxide, thiocyanate, sulfate and cyanate have been followed and a simple kinetic model is proposed based on simultaneous evaluation of all the concentration–time series detected. It was clarified that intermediates (O_xSCN^-, whereas $x=1$, 2 and 3) could not be detected with routine HPLC and CE techniques due to their relatively short lifetimes even in weakly alkaline conditions. Further quantitative determination and evaluation procedure revealed that buffers strongly affect the rate of reaction in the order of ammonia, phosphate, carbonate and borate, but the overall rate law with respect to the formal kinetic order of the reactants remained untouched regardless of the quality of the buffer components applied. It is well-known that HPLC and CE techniques are very useful tools to elucidate the kinetics and mechanism of those reactions where the experimental conditions can be chosen such a way that the separation process does not influence the reaction rate and mechanism to be studied. If these conditions are fulfilled then not only the concentration of the reactants and end-products but also that of key intermediates could be detected simultaneously that is able to easily set up a correct kinetic model or mechanism. However routine usage without doublechecking the seemingly new results should be avoided because it may sometimes lead to serious misinterpretation.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2013.11.076.

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