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Published online in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/bio.705 *ORIGINAL RESEARCH*

Studies of visible oscillating chemiluminescence with a luminol–H_2O_2–KSCN–$CuSO_4$–NaOH system in batch reactor

Abdolraouf Samadi-Maybodi* and S. M. Ourad

Department of Chemistry, Faculty of Basic Science, Mazandaran University, Babolsar, Iran

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ABSTRACT: Oscillating chemical reactions are complex systems involving a large number of chemical species. In oscillating chemical reactions some species, usually reaction intermediates, exhibit fluctuation in concentration. Visible oscillating chemiluminescence, produced by the addition of luminol (3-aminophthalhydrazide) to the oscillating system H_2O_2–KSCN–$CuSO_4$–NaOH, was investigated. In this study the effect of varying the concentration of H_2O_2, KSCN, $CuSO_4$, NaOH and luminol was investigated in a batch reactor. We showed that the concentration of all components involved in the oscillating chemilumenscent reaction influenced the light intensity and the oscillation period. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: visible oscillating chemiluminescence; luminol; batch reactor

INTRODUCTION

Oscillating chemical reactions are dynamic systems that have traditionally aroused interest in the context of kinetic methods of analysis (1–6). The reactions are complex systems involving a large number of chemical species that react via unusual mechanisms. Oscillations in the concentrations of reaction intermediates arise when a chemical reaction that is kept far from equilibrium interacts via coupled feedback steps. Applications of oscillating reactions in chemistry have grown substantially in the last few years.

A well-known oscillating reaction is the Belousov–Zhabotinskii reaction, which involves the oxidation of an organic compound (e.g. malonic acid) by bromate ions in a strongly acidic aqueous medium (7). This reaction is catalysed by traces of transition metal ions that contain two oxidation states, differing in a single electron, whether in free form [e.g. Ce(III)-Ce (IV), Mn(II)–Mn(III)] or as complexes [e.g. Ru $(bpy)_3{}^{2+}$–$Ru(bpy)_3{}^{3+}$] (8). According to Epstein *et al.*, the mechanism by which the oscillating reaction takes place consists of 30 kinetic steps involving 26 independent variables and thus requires some further investigation (9–11).

The sharp pulses of blue light ($\lambda = 424$ nm) produced by the addition of luminol to the oscillating system H_2O_2–KSCN–$CuSO_4$–NaOH are unlike oscillations characteristic of this system. The light-generating reaction of luminol has been the subject of much research (12). In basic aqueous solution, chemiluminescence results from the oxidation of luminol by hydrogen peroxide catalysed by a transition-metal ion, such as copper or cerium.

Typical oscillation attributes, such as the oscillation period and amplitude, were recently used to evaluate their use in chemical analysis (13, 14), since the oscillating period and amplitude depend strongly on the concentrations of the reaction ingredients (15).

In this study, the oscillating period and amplitude were studied in the luminol–H_2O_2–KSCN–$CuSO_4$–NaOH system in a batch reactor. We performed a series of experiments in which, for each series, the concentrations of one of the species was varied and the other ones were held constant.

*Correspondence to: A. Samadi-Maybodi, Department of Chemistry, Faculty of Basic Science, Mazandaran University, Babolsar, Iran.
Email: samadi@umz.ac.ir

MATERIALS AND METHODS

Reagents

Stock solutions were prepared from commercially available reagent-grade potassium thiocyanate (Merck), 30% hydrogen peroxide, sodium hydroxide, copper sulphate pentahydrate and luminol without further purification. Bi-distilled water was used throughout.

Apparatus

The oscillating reaction was monitored with a home-made apparatus equipped with a Model BPY47 photocell (Leybold, Huerth, Germany). The apparatus was connected to a personal computer via an interface (Micropars, Tehran, Iran). Experiments were carried out with magnetic stirring (500 rpm) in a 15 mm diameter light-tight flat-bottomed glass cell at 24 ± 1 °C. The time resolution of the apparatus is 0.6 s and CL intensity is reported in relative units.

Procedures

In the reaction vessel of the batch were placed 200 µL NaOH (0.15 mol/L), 100 µL KSCN (0.20 mol/L), 200 µL H_2O_2 (3.2 mol/L), 200 µL $CuSO_4$ (0.01 mol/L) and 100 µL luminol (6×10^{-2} mol/L in 0.15 mol/L NaOH) and bi-distilled water was added up to a final volume of 3 mL. The experiment was carried out with shaking (rpm = 500) and light emission monitored during the oscillating reaction. In each series of experiments, the concentration of only one of the species was varied whilst holding the others constant. The order of addition and the final volume for all experiments were the same.

RESULTS AND DISCUSSION

The reaction between hydrogen peroxide and sodium thiocyanate in alkaline medium is catalysed by copper(II) and is first-order in each reactant (10, 16).

$$4H_2O_2 + SCN^- \longrightarrow HSO_4^- + NH_4^+ + HCO_3^- + H_2O \quad (1)$$

The rate-determining step is:

$$H_2O_2 + SCN^- \longrightarrow HOSCN + OH^- \quad (2)$$

It is proposed that the SCN^-, acts to separate in time the steps in which copper(I) forms and is temporarily stabilized by SCN^-. It is then reoxidized to the bivalent state with the simultaneous oxidation of the SCN^- However, recent studies (10) have revealed the occurrence of other intermediates, such as: cyanosulphite, $^-OS(O)CN$; peroxocyanosulphite, $^-OOS(O)CN$; hypothiocyanite, ^-OSCN; and peroxohypothiocyanate ions, ^-OOSCN.

Luminol concentration

The effect of luminol on the H_2O_2–KSCN–CuSO4–NaOH oscillating system was studied in a series of experiments with different concentrations of luminol and constant concentrations of NaOH, KSCN, Cu(II) and hydrogen peroxide in a batch reactor. This experiment was performed with final luminol concentrations of 2.4×10^{-3}, 4.8×10^{-3}, 7.3×10^{-3}, 9.8×10^{-3} and 1.2×10^{-2} mol/L and constant concentrations of H_2O_2, KSCN, Cu(II) and NaOH (2.6×10^{-1}, 5.8×10^{-3}, 5.3×10^{-4} and 4.4×10^{-2} mol/L, respectively).

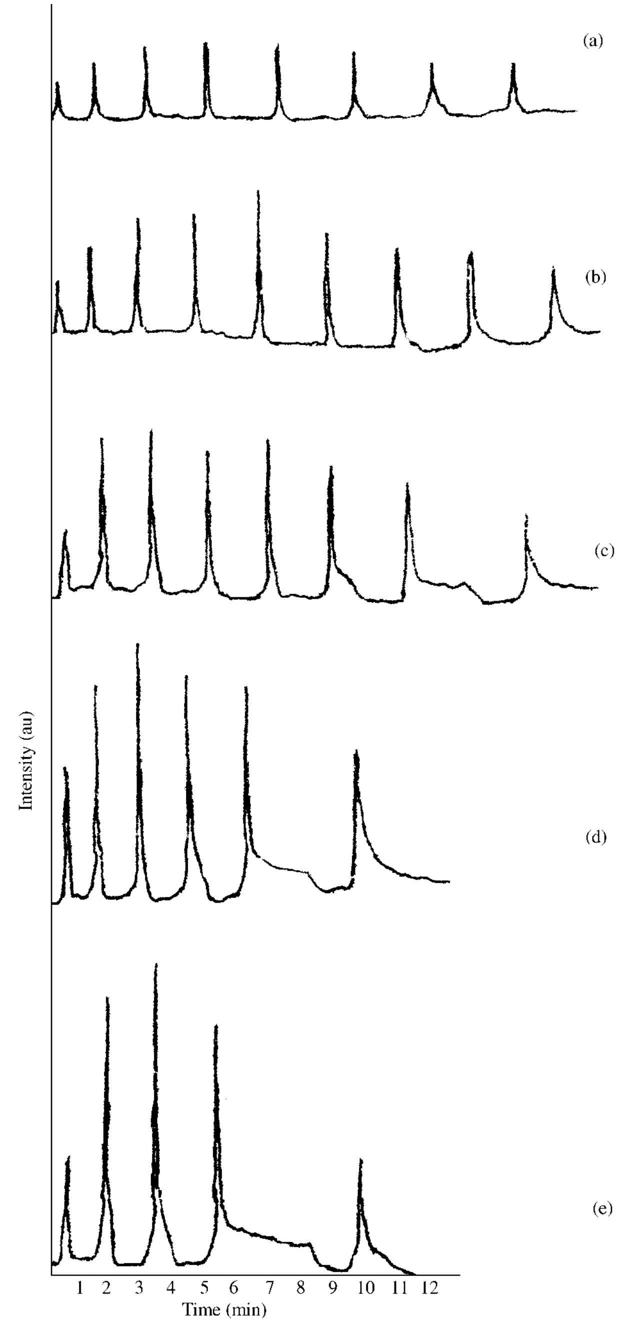

Figure 1. Temporal evolution of oscillating chemiluminescence for the luminol–H_2O_2–KSCN–$CuSO_4$–NaOH system in a batch reactor with different concentrations of luminol [(a) 2.4×10^{-3}; (b) 4.8×10^{-3}; (c) 7.3×10^{-3}; (d) 9.8×10^{-3}; and (e) 1.2×10^{-2} mol/L; with constant concentration of H_2O_2, 2.6×10^{-1} mol/L; KSCN, 5.8×10^{-3} mol/L; Cu(II), 5.3×10^{-4} mol/L and NaOH, 4.4×10^{-2} mol/L].

Luminol influences on the intensity of light emission from the oscillating system chemiluminescence as shown in Fig. 1. An increase in the luminol concentration decreased the period of the oscillation. The overall time of oscillation is also affected by the concentration of

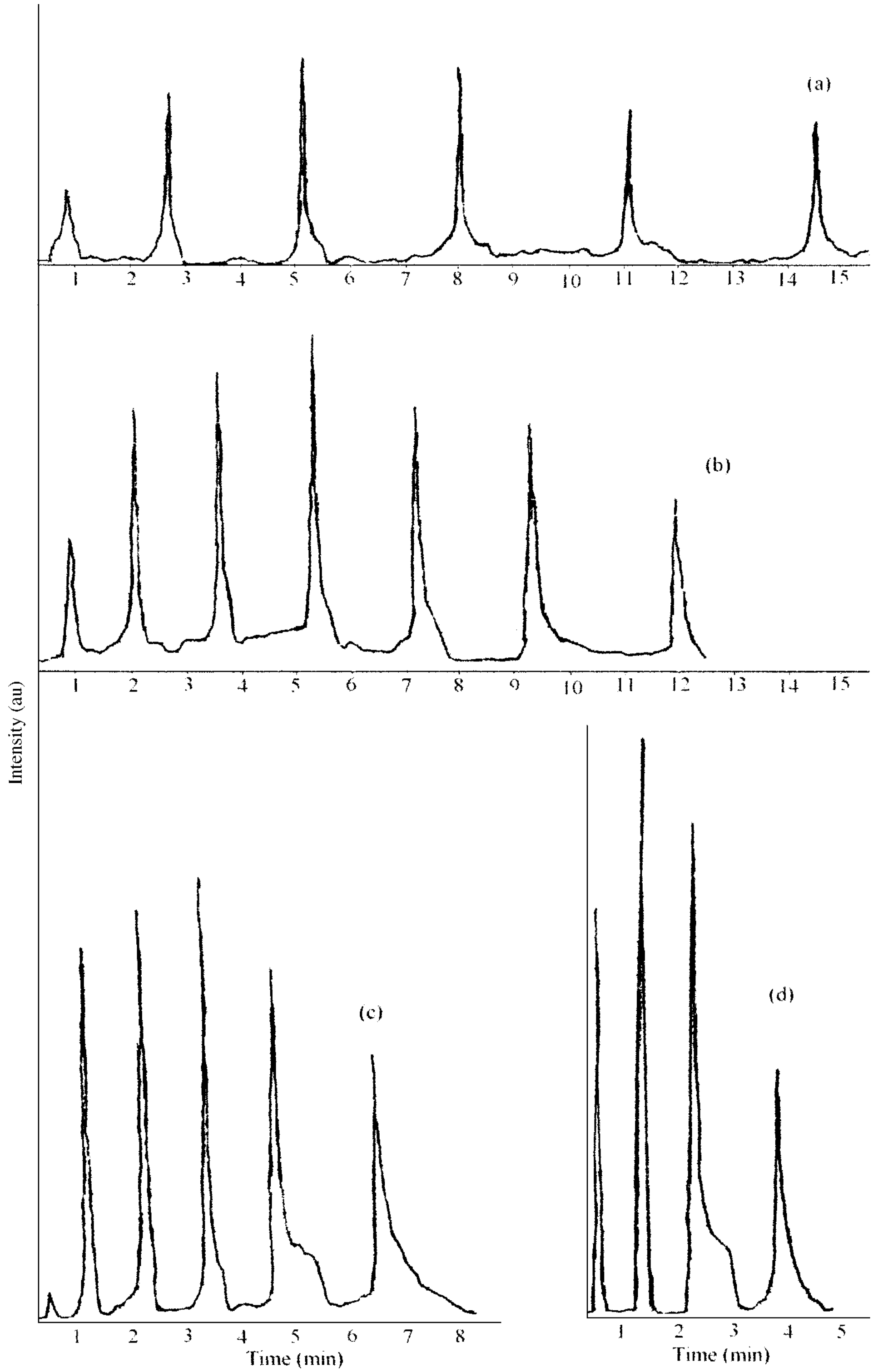

Figure 2. Temporal evolution of oscillating chemiluminescence for the luminol–H_2O_2–KSCN–$CuSO_4$–NaOH system in a batch reactor with different hydrogen peroxide concentrations [(a) 0.15; (b) 0.30; (c) 0.45; and (d) 0.60 mol/L: with constant concentration of KSCN, 5.8×10^{-3} mol/L; Cu(II), 5.3×10^{-4} mol/L; NaOH, 4.4×10^{-2} mol/L; and luminol, 7.3×10^{-3} mol/L].

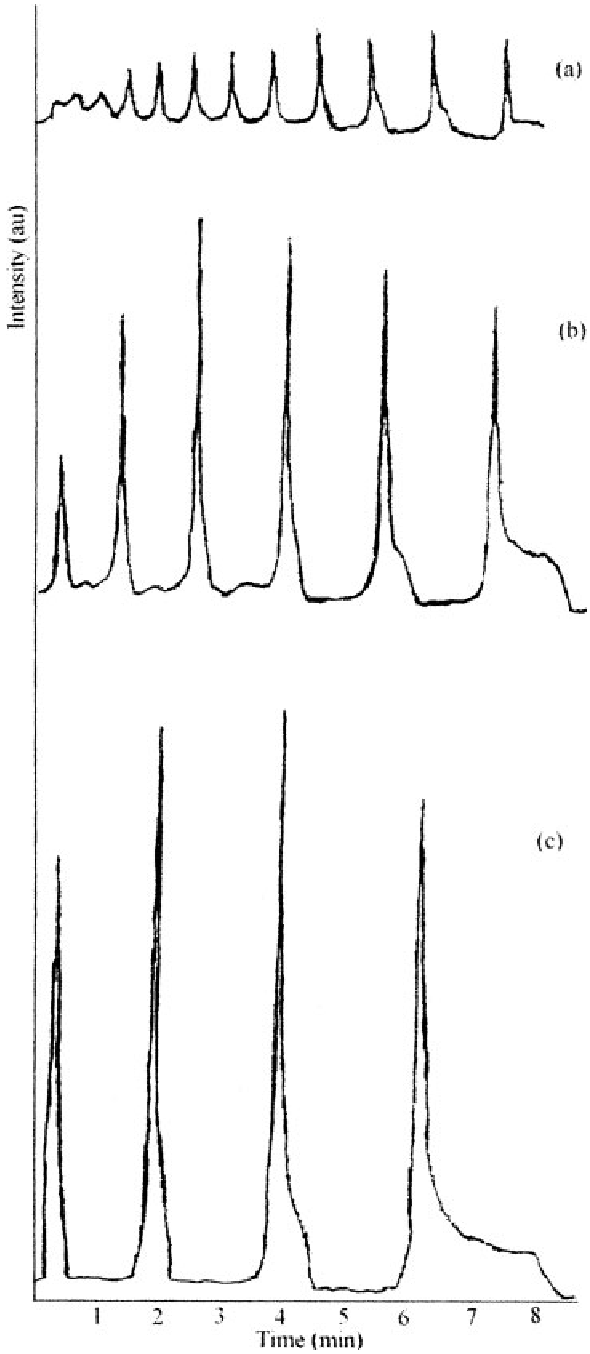

Figure 3. Temporal evolution of oscillating chemiluminescence for the luminol–H_2O_2–KSCN–$CuSO_4$–NaOH system in a batch reactor with different potassium thiocyanate concentrations [(a) 2.60×10^{-2}; (b) 5.86×10^{-2}; and (c) 8.00×10^{-2} mol/L: with constant concentrations of $CuSO_4$, 5.3×10^{-4} mol/L; NaOH; 4.4×10^{-2} mol/L; luminol, 7.3×10^{-3} mol/L; and H_2O_2, 2.6×10^{-1} mol/L].

luminol. Increasing the luminol concentration decreases the oscillating chemiluminescence period; however, the intensity of light emitted is enhanced. It should be noted that no appreciable changes in pulse duration (i.e. the half-width of light pulses) were observed at different luminol concentrations.

Hydrogen peroxide concentration

The influence of the H_2O_2 was assessed with different concentrations of H_2O_2 (0.15, 0.30, 0.45 and 0.60 mol/L) but constant concentration of NaOH, KSCN, Cu(II) and luminol (with 5.8×10^{-3}, 5.3×10^{-4}, 4.4×10^{-2} and 7.3×10^{-3} mol/L, respectively) in the batch reactor.

The oscillating chemiluminescence patterns obtained at the different H_2O_2 concentrations are illustrated in Fig. 2. Changing concentration of H_2O_2 influenced both light amplitude and the period of oscillation. Increasing the concentration of H_2O_2 decreased the oscillation period significantly.

Potassium thiocyanate concentration

The potassium thiocyanate concentration was investigated in the batch reactor at concentrations of 2.60×10^{-2}, 4.00×10^{-2}, 5.86×10^{-2}, 8.00×10^{-2} and 1.2×10^{-1} mol/L, but constant concentrations of $CuSO_4$, NaOH, luminol and H_2O_2 (5.3×10^{-4}, 4.4×10^{-2}, 7.3×10^{-3} and 2.6×10^{-1} mol/L, respectively). The effect of thiocyanate on the oscillating chemiluminescence reaction is shown in Fig. 3. As can be seen, increasing the concentration of thiocyanate caused the number of oscillations to decrease significantly, but the intensity of the emitted light is increased. Results obtained from this experiment indicate that the intensity as well as oscillation period varies much more strongly with the thiocyanate concentration than the other reaction components.

Copper concentration

The effect of copper concentration was performed with final concentrations of 2.44×10^{-4}, 3.52×10^{-4}, 5.28×10^{-4}, 7.04×10^{-4} and 8.8×10^{-4} mol/L, but constant concentrations of NaOH, luminol, H_2O_2 and KSCN (4.4×10^{-2}, 7.3×10^{-3}, 2.6×10^{-1} and 5.8×10^{-3} mol/L, respectively) in the batch reactor. Fig. 4 shows that the copper concentration significantly influences the behaviour of the oscillating reaction. Increasing concentration of Cu(II) caused both the light intensity and the oscillating amplitude to decrease. The total period of emitted light is the same, i.e. 15 min, but the number of light pulses was increased by increasing the copper concentration.

Sodium hydroxide concentration

The effect of sodium hydroxide concentration was performed with final concentrations of 8.8×10^{-3}, 1.1

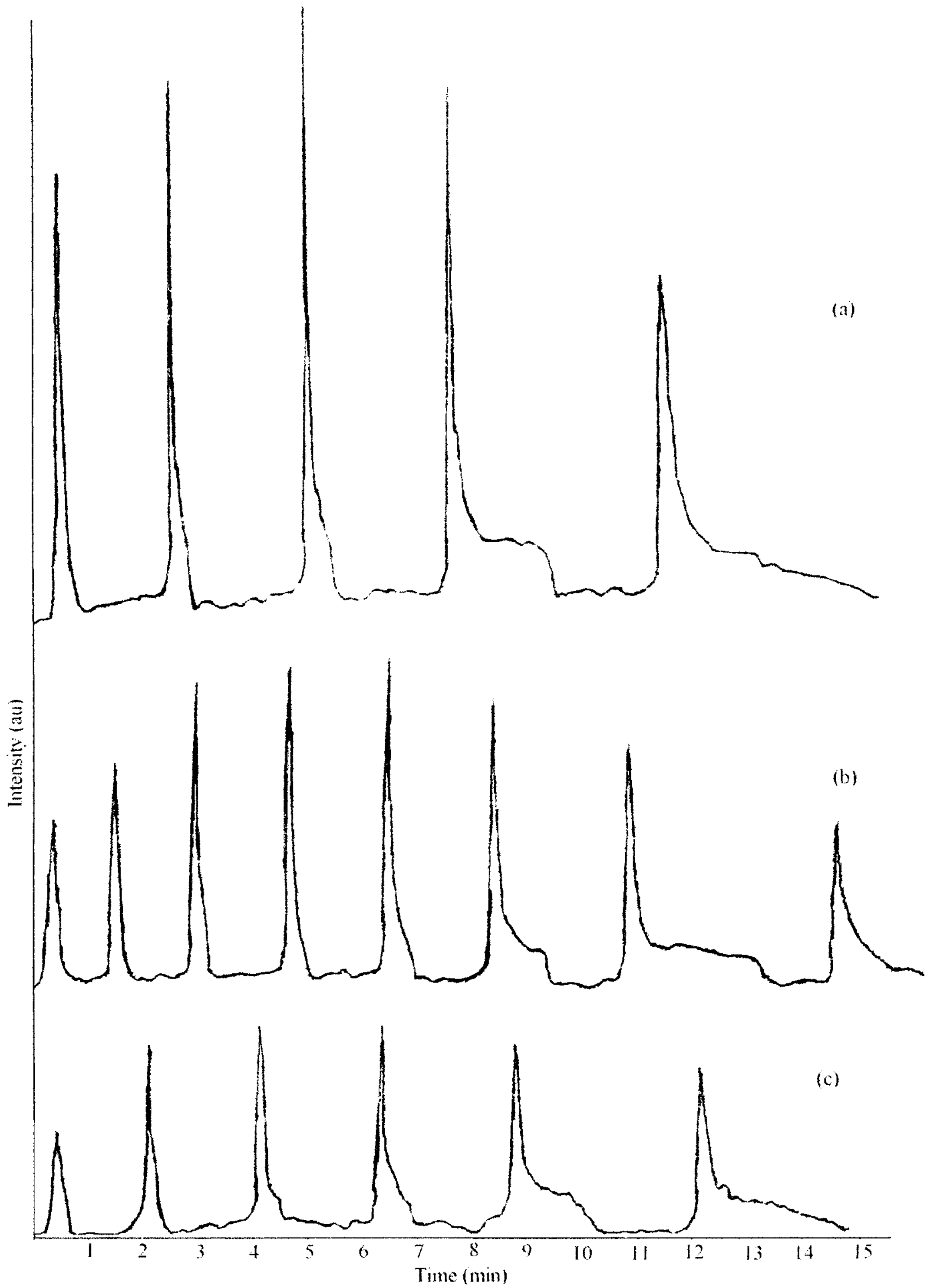

Figure 4. Temporal evolution of oscillating chemiluminescence for the luminol–H_2O_2–KSCN–$CuSO_4$–NaOH system in a batch reactor with different concentrations of copper(II) [(a) 2.44×10^{-4} mol/L; (b) 5.28×10^{-4} mol/L; and (c) 8.8×10^{-4} mol/L: and constant concentrations of NaOH, 4.4×10^{-2} mol/L; luminol, 7.3×10^{-3} mol/L; H_2O_2, 2.6×10^{-1} mol/L; and KSCN, 5.8×10^{-3} mol/L].

$\times 10^{-2}$, 1.7×10^{-2}, 3.5×10^{-2} and 5.3×10^{-2} mol/L and constant concentrations of H_2O_2, KSCN, Cu(II) and luminol (2.6×10^{-1}, 5.8×10^{-3}, 5.3×10^{-4} and 7.3×10^{-3} mol/L, respectively. Fig. 5 shows that the oscillation period and the number of light pulses were increased by increasing concentration of sodium

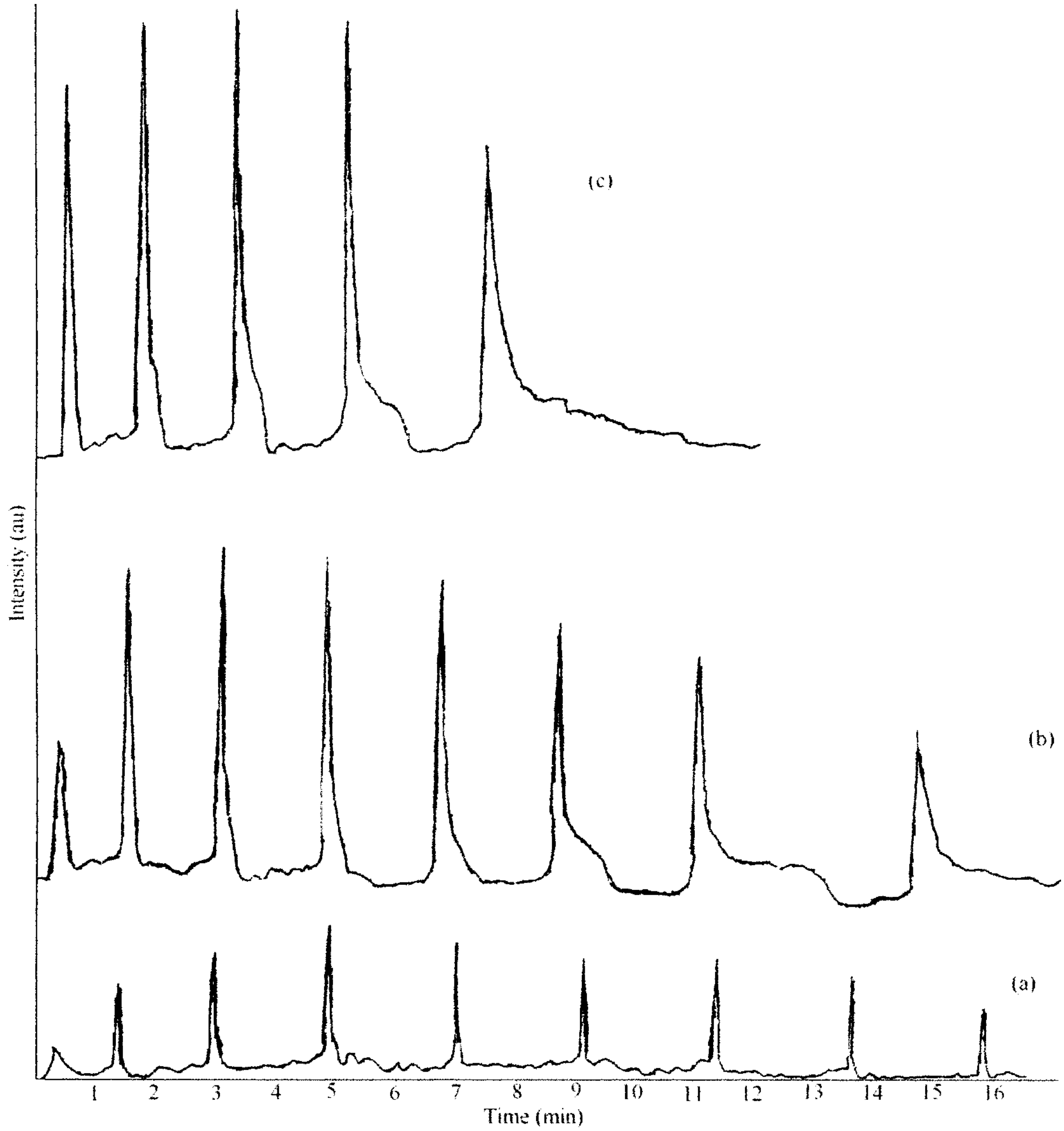

Figure 5. Temporal evolution of oscillating chemiluminescence for the luminol–H_2O_2–KSCN–$CuSO_4$–NaOH system in a batch reactor with different concentrations of sodium hydroxide. [(a) 8.8×10^{-3} mol/L; (b) 1.1×10^{-2} mol/L; (c) 5.3×10^{-2} mol/L; with constant concentrations of luminol, 7.3×10^{-3} mol/L; H_2O_2, 2.6×10^{-1} mol/L; KSCN, 5.8×10^{-3} mol/L; and Cu(II) 5.3×10^{-4} mol/L].

hydroxide, but increasing concentration of sodium hydroxide decreased the light amplitude.

CONCLUSION

The present study indicates that the concentration of all components involved in the oscillating chemilumenscence influence the oscillation period, light amplitude and total time of emitted light. However, KSCN and Cu(II) were found to have the greatest influence on the oscillating reaction.

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