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Luminescent Chemical Waves in the Cu(II)-Catalyzed Oscillatory Oxidation of SCN⁻ Ions with Hydrogen Peroxide

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The oscillatory oxidation of thiocyanate ions with hydrogen peroxide, catalyzed by Cu^{2+} ions in alkaline media, was so far observed as occurring simultaneously in the entire space of the batch or flow reactor. We performed this reaction for the first time in the thin-layer reactor and observed the spatiotemporal course of the above process, in the presence of luminol as the chemiluminescent indicator. A series of luminescent patterns periodically starting from the random reaction center and spreading throughout the entire solution layer was reported. For a batch-stirred system, the bursts of luminescence were found to correlate with the steep decreases of the oscillating Pt electrode potential. These novel results open possibilities for further experimental and theoretical investigations of those spatiotemporal patterns, including studies of the mechanism of this chemically complex process.

1. Introduction

Since the discovery of the spatiotemporal patterns in the Belousov−Zhabotinskii (BZ) reaction,[1] the formation of chemical waves remains the subject of interest in the studies of chemical dissipative systems (see, e.g., ref 2). Other well-known examples of chemical waves include, among others, similar patterns observed in the chlorite−iodide−malonic acid system[3] and the traveling fronts reported for the Landolt-type reaction between iodate(V) ions and arsenic(III) acid.[4,5] Of other systems, those involving hydrogen peroxide have been some of the most intensively studied homogeneous oscillatory processes. Besides the classical Bray[6] and Briggs−Rauscher[7] processes, one should note the more recent studies of the oscillatory interaction of H_2O_2 with the sulfur-containing reducing agents, such as, for example, sulfides,[8] sulfites,[9] thiosulfates,[10,11] or thiocyanates.[12,13] The latter, $H_2O_2-SCN^--OH^-$ oscillatory/bistable system, requiring Cu^{2+} ions as a catalyst, seems to be unique. First, this is a rare example of the system in which oscillations can appear spontaneously in both the flow and batch reactors.[12] Second, these oscillations appear to occur only around one of two possible steady states,[12] contrary to other numerous systems in which oscillations involve switching between the two steady states (cf. Boissonade and De Kepper[14] model).

The main reactions occurring in the $SCN^--H_2O_2-OH^--Cu^{2+}$ oscillatory system[12]

$$4H_2O_2 + SCN^- \rightarrow HSO_4^- + HOCN + 3H_2O \qquad (1)$$

$$HOCN + 2H_2O \rightarrow NH_4^+ + HCO_3^- \qquad (2)$$

do not reflect the complex mechanism of this process for which Orbán et al.[13] have proposed so far 30 steps involving 23 intermediates. The yellow color of the solution presumably[12] originates from the copper(I) intermediates, such as, for example, peroxide CuOOH, the concentration of which changes periodically during the oscillations.

Because all of these studies refer to the batch or flow, continuously stirred reactors (CSTR), it became our aim to check whether this atypical oscillatory/bistable system can also produce spatial or spatiotemporal patterns in the immobilized (unstirred) thin layer of the solution.

2. Experimental Section

All reagents used were of analytical grade (p.a. = pure for analysis). P.a. NaSCN (Fluka, Poland), p.a. NaOH (Merck, Germany), p.a. 95% (w/w) H_2SO_4 (POCh, Poland), p.a. $CuSO_4$ (POCh, Poland), and p.a. 30% H_2O_2 (Chempur, Poland) were used without further purification. In the experiments with p.a. luminol (5-amino-2,3-dihydro-1,4-phthalazinedione) $C_8H_7N_3O_2$ (Roth, Germany), its 5 mM stock solution in 0.1 M NaOH was used. Silica gel, fumed (particle size 0.007 μm, 390 ± 40 $m^2\ g^{-1}$) manufactured by Sigma, was used for enhancing the viscosity of the reaction medium. For all solutions triply distilled water, additionally purified in a final step using Millipore filters, was used.

Potentiometric experiments were performed with a Hewlett-Packard 7090A multichannel Measurement Plotting System. The platinum plate ($A = 0.6\ cm^2$) worked as the indicator electrode. The reference electrode Ag|AgSCN|0.1 M NaSCN was separated from the studied solution with a salt bridge, filled with 0.1 M NaSCN. The content of the glass batch reactor ($V = 25\ cm^3$) was stirred with a magnetic stirrer PM TYPE MM 6 (Poland).

The luminescent spatiotemporal patterns were observed in the thin-layer reactor, assembled from the two round glass plates of a diameter $\Phi = 79$ mm, between which the reacting solution was placed (the lack of the free solution surface excluded the

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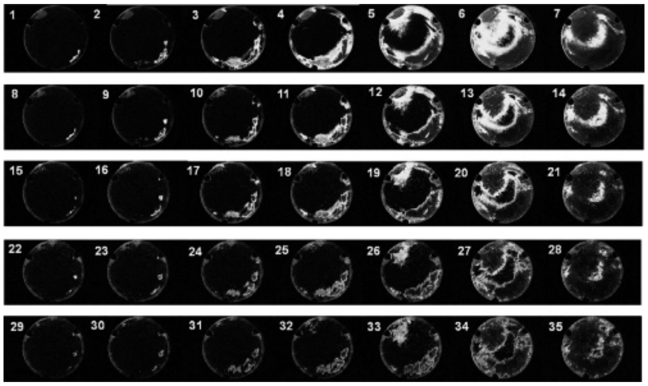

Figure 1. Luminescent chemical waves in the thin layer of the solution (d = 1.29 mm), in which the Cu^{2+}-catalyzed oxidation of SCN^- with H_2O_2 occurred. Particular pictures were taken at the times shown in Figure 2. Initial concentrations (M): $[NaSCN]_0 = 0.051$, $[NaOH]_0 = 0.045$, $[H_2O_2]_0 = 0.34$, $[CuSO_4]_0 = 2.1 \times 10^{-4}$, $[\text{luminol}]_0 = 5.46 \times 10^{-4}$. Exposure time = 10 s.

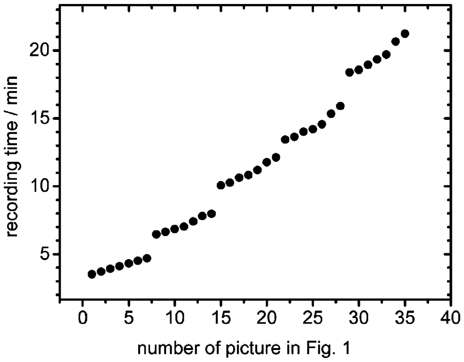

Figure 2. Correlation between the number of the picture in Figure 1 and the recording time measured from the moment of mixing the reagents. The time intervals between the successive sections correspond to dark solutions, the digital pictures of which are not included.

Bénard−Marangoni instabilities). The distance, d, between the plates (i.e., the thickness of the solution layer) was varied from 230 μm to 2.00 mm.

The images of the luminescent waves were taken using the Nikon D70 and Nikon Coolpix E5700 digital reflex cameras with the resolutions of 6 million and 5 million pixels, respectively. Because for most pictures the intensity of the blue luminescence was rather weak, the contrast of original digital images was enhanced using Corel PhotoPaint ver. 12 (2004 Corel Corp.) and ACDSee Photo Editor ver. 4.0 (2006 ACD System, Ltd.) software, without any modification of the essential morphology of the reported patterns.

Measurements of the luminescence intensity in the stirred batch reactor were performed with the homemade device, consisting of the 3V solar panel, connected to the circuit amplifying the solar cells voltage for the factor of 100. All experiments were performed at an ambient temperature of 294 ± 0.5 K.

3. Results and Discussion

Because of a very low intensity of a yellow color of the $NaSCN-H_2O_2-NaOH-CuSO_4$ mixture in the thin layer, it was not possible to distinguish visually the colored from the colorless zones of the thin solution layer, during the course of the reaction. However, according to Sattar and Epstein,[15] as well as Orbán,[16] the presence of luminol in the stirred $KSCN-KOH-H_2O_2-CuSO_4$ system should cause periodic bursts of weak blue luminescence (see also ref 17). Following these reports, to the freshly prepared solution of NaSCN, NaOH, H_2O_2, and luminol (mixed in the given order), we added an appropriate portion of the $CuSO_4$ solution and, immediately after careful mixing, the portion of this solution was poured between the glass plates of the thin-layer reactor. Within 1−2 min, in the darkroom, we noticed a local zone of weak blue luminescence, which soon developed into more complex luminescent traveling waves.

The very interesting feature of these phenomena was that once prepared solution yielded spontaneously a ***reproducible*** series of periodically changing luminescent patterns, starting in each series from *the same* zone of the system. This is proven by the representative series of pictures (taken with the digital camera) shown in Figure 1. The arrangement of these pictures (similar structures are placed in the same columns) shows the striking periodicity and remarkable stability in the evolution and decay of the structures that lasted for more than half an hour. This system thus behaves differently than, for example, the BZ reaction, for which one observes the continuous random nucleation of chemical waves and, in order to reset these patterns, one has to homogenize the system. The different behavior of our system may be due, among others, to the fact that the oscillations occur around one steady state, but further analysis, including numerical modeling, is required to decide whether the observed luminescent waves are of the trigger or phase type.[2]

The correlation between the number of a given picture and the corresponding recording time is given in Figure 2.

Repetitions of these experiments with the next fresh samples of the same starting solution yielded the same number of the periodically occurring sequences of structures, which was 5 within 24 min. Of course, every new series of periodically changing patterns started from another, random site in the solution layer.

For the better visualization of the structure of the chemical waves from Figure 1, the three exemplary, enlarged pictures are collected in Figure 3.

Figure 4 shows the correlation between the bursts of luminescence and the oscillatory potential changes for the platinum electrode, recorded for the sample of similar initial reagents concentrations, as for the observation of the waves. The sharp and narrow peak of luminescence appears when the potential of the Pt electrode sharply decreases.

According to a known mechanism of chemiluminescence of luminol in an alkaline medium,[18,19] it is clear that the luminescent zones in our thin-layer reactor should indicate a relatively high local concentration of oxygen. Literature reports obtained with the use of the batch reactor coupled with the mass spectrometer[12] suggest, however, that the maximum rate of production of oxygen occurs not when the Pt electrode potential decreases sharply (and when the burst of luminescence is observed by us, cf. Figure 4) but a bit later, when the Pt potential increases after the peak value. Nevertheless, without detailed, future studies it is now difficult to correlate these phenomena very accurately. If the literature studies on the production of oxygen reported, let us assume, a bit delayed response, because the gas driven out of the reaction mixture has to pass a certain distance to reach the mass spectrometer, then a slight phase shift may occur between various oscillatory responses. In view of this it seems that, compared to the mass spectrometry, luminol may serve as a "quicker" indicator for the local enhancement of oxygen concentration, provided that the evolution of chemiluminescence is very fast. In fact, typical experimental practice shows that this luminescence appears immediately if the initially separated solutions of (luminol + NaOH) and ($K_3[Fe(CN)]_6$ + H_2O_2) are brought into contact.[18]

Figure 3. Enlarged images of the selected luminescent patterns (in natural blue color) from Figure 1: from top to bottom no. 3, no. 5, and no. 20. Numerous small bright points, particularly well visible on the bottom image, denote small bubbles of oxygen evolving as one of the reaction products.

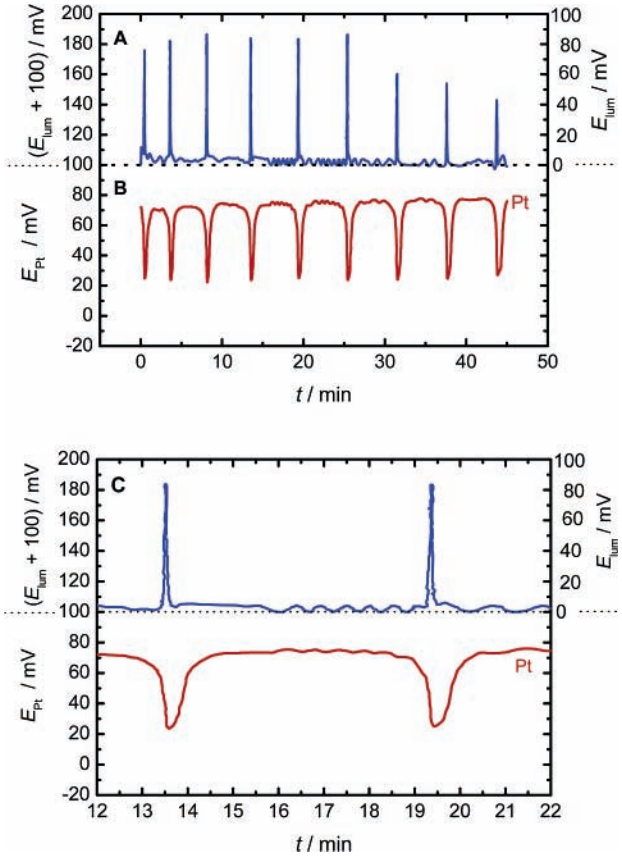

Figure 4. Correlation of the changes of the luminescence intensity (A) with the changes of the Pt electrode potential (B) as a function of time for the oscillatory oxidation of SCN^- with H_2O_2 in the stirred batch reactor. (C) Expanded fragment of the A and B plots showing that the maximum luminescence intensity corresponds to the negative slope of the potential peak recorded for the Pt electrode. Initial concentrations (M): $[NaSCN]_0 = 0.052$, $[NaOH]_0 = 0.044$, $[H_2O_2]_0 = 0.29$, $[CuSO_4]_0 = 1.8 \times 10^{-4}$, $[luminol]_0 = 4.7 \times 10^{-4}$. Temperature: 294.2 K. E_{lum}: the amplified solar cell voltage, proportional to the intensity of luminescence; in order to avoid overlapping of the $E-t$ courses, the measured E_{lum} values were in the plot increased for 100 mV.

Some factors could, but rather slightly, affect the shapes of the reported patterns. Because of a low intensity of emitted blue light, the photographic exposure time had to be prolonged up to 10 s, however short enough to catch any individual, only slightly blurred moving pattern. Furthermore, although the formation of bubbles of oxygen as one of the products could cause expansion of a liquid layer and thus partial deformation of the observed structures, this effect appeared to be practically insignificant under the conditions of our experiments. Also, in view of the previous works (cf. e.g., refs 2 and 20−22) it is useful to consider the eventual effect of convection, caused by buoyancy forces, on the morphology of the studied patterns. Our additional experiments proved that upon addition of superfine silica gel (2−10%, w/w) enhancing the viscosity of the medium, one observes similar luminescent structures, the development of which also exhibits periodicity (see Figure 5, top row). However, with respect to aqueous solutions we reported the following differences: (i) the formation of the structures involved periodic, prolonged appearance of bright uniform luminescence and (ii) the pattern formation ended after only 10−12 min with the uniform bright luminescence emitted by the entire layer. Our comparative measurements of Pt electrode potential changes, recorded in the batch, stirred system of the same composition (i.e., also including both luminol and

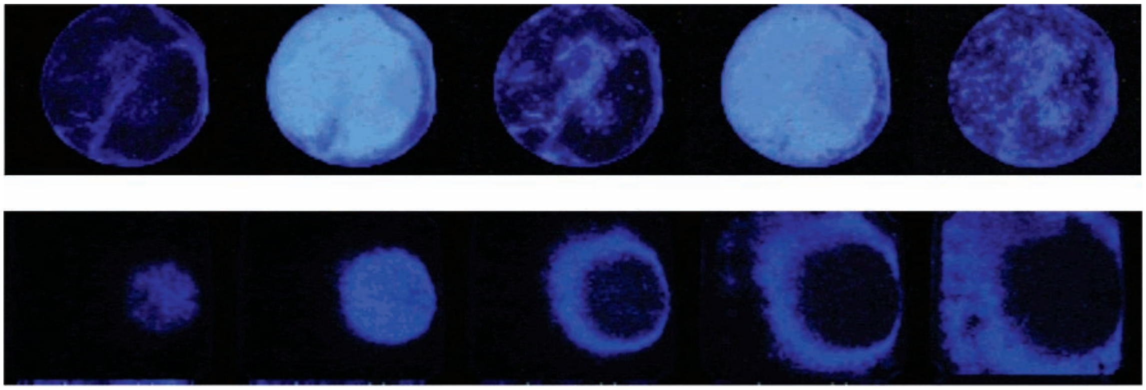

Figure 5. Top row: Periodicity of spatiotemporal luminescent patterns in the medium of the viscosity enhanced by addition of silica gel (9.1% w/w); $d = 2.00$ mm; from left to right: $t = 120$, 154, 382, 430, and 740 s from the moment of mixing the reagents; exposure time 8 s. Bottom row: The development of a concentric wave in the system with no gel added, $d = 2.00$ mm, series of five pictures taken every 8 s after $t = 282$ s from the moment of mixing the reagents. Exposure time = 8 s.

silica gel) showed a good correlation between the characteristics of the batch and thin-layer systems: in the batch reactor, the oscillatory peaks became remarkably wider at relatively low Pt potentials, associated with the burst of luminescence (cf. Figure 4) and the entire oscillatory course also finished after 10−12 min. This means that silica gel is not a completely inert component of the system and modifies the oscillation's shape and lifetime both in the absence and in the presence of (then forced) convection. Further experiments with aqueous solutions of varying layer width led to rather ambiguous results; for example, for the width $d = 460$ μm, the wave fronts similar to those shown in Figure 1 developed, whereas for the greater width $d = 2.00$ mm, other structures including single rings appeared (cf. Figure 5, bottom row). In our opinion, with respect to the role of convection the results with silica gel are more reliable and they suggest that although the convection due to buoyancy forces may slightly modify our patterns in aqueous media, it is not decisive for their formation; so, the phenomena shown in Figures 1 and 3 are not purely or even predominantly convective structures. The eventual effect of convection on the structures shown in the bottom row of Figure 5 requires further studies.

In conclusion, the formation of the spatiotemporal structures in the $SCN^-{-}H_2O_2{-}OH^-{-}Cu^{2+}$ oscillatory reaction is a novel result. These patterns are significantly different from a set of randomly nucleating and concentrically developing fronts, sometimes also taking a spiral form (cf., e.g., ref 23), which have been reported, as mentioned above, for the Belousov−Zhabotinskii or the chlorite−iodide−malonic acid system. Instead, our luminescent patterns resemble the theoretically calculated dissipative concentrations fronts in the model reaction scheme: Brusselator coupled with diffusion.[24,25]

The research will be continued in the direction of further studies of the spatiotemporal patterns in the $H_2O_2{-}NaSCN{-}NaOH{-}CuSO_4$ system and the mechanism of this complex redox process.

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