Kinetics and Catalysis, Vol. 42, No. 5, 2001, pp. 606–608. Translated from Kinetika i Kataliz, Vol. 42, No. 5, 2001, pp. 670–672.
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New Oscillatory Process in Aqueous Solutions of Compounds Containing Carbonyl and Amino Groups[1]

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Received July 20, 2000

Abstract—Frequency-correlated oscillations of chemiluminescence and the redox potential are observed during the amino-carbonyl reaction, which occurs in aqueous solutions of methylglyoxal and various amino-containing compounds (ethanolamine, glycine, and β-alanine) at room temperature. The duration and amplitude of oscillations depend on the composition and concentration of the starting reactants, pH, stirring, and surface area through which oxygen diffuses into the system.

INTRODUCTION

Despite many studies of oscillatory chemical systems (see review [1]), information on the detection and study of aqueous oscillatory systems involving the nonenzymatic oxidation of organic compounds by molecular oxygen are very scarce and incomplete [2–4]. However, it is evident that detailed studies of these systems would lead to considerable progress in understanding the mechanisms of functioning of more complex biosystems.

The majority of oscillatory reactions known to date involve activator–inhibitor subsystems in which the activator can be reproduced autocatalytically. In distributed nonlinear systems without stirring, the presence of such subsystems can result in the spontaneous formation of stationary dissipative structures and wave processes [5].

The amino-carbonyl reaction (the Maillard reaction [6]) is a complex multistep process that occurs through the formation of Schiff bases and high-molecular colored compounds (melanoidines) [7, 8]. However, it is known that products capable of reacting with molecular oxygen are already formed at the very first steps of the amino-carbonyl reaction [9]. In this work, we present for the first time data on chemiluminescence and redox potential oscillations during amino-carbonyl reactions in the aqueous alkaline solutions of methylglyoxal and various amino-containing compounds at room temperature.

EXPERIMENTAL

Aqueous solutions of methylglyoxal (INC Pharmaceuticals) in an alkaline buffer (carbonate buffer at pH 9.5–10.9, phosphate buffer at pH 11.0–11.9) were mixed with aqueous solutions of amino compounds (ethanolamine (Merck), glycine, β-alanine (Sigma)). Using NaOH solutions, pH was set to a required value. All solutions were prepared with distilled deionized water purified by Milli-Q technology (Millipore).

The solutions obtained were poured into cylindrical flasks from various materials to exclude the surface effect. Samples, which contacted with atmospheric air, were mounted either directly in a chamber of a Mark II (Nuclear Chicago) liquid scintillation counter or in a chamber designed by us to make it possible to work with large volumes of samples. Chemiluminescence was detected using an EMI 9750QB/1 photomultiplier tube (with sensitivity ranging from 300 to 600 nm and a maximum sensitivity at 420 nm) in the single photon counting mode with a high temporal resolution of 0.1 min for several hours at room temperature. Redox potentials were measured by a platinum electrode with reference to an Ag/AgCl electrode at intervals of 0.1 min on an Ekspert-001-2.0.1 instrument (with an accuracy of ±0.2 mV) (Russia). The concentration of dissolved oxygen was determined by the amperometric method using the Clark electrode.

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[1] Proceedings of the II All-Russia Workshop on Highly Organized Catalytic Systems (Moscow, June 27–30, 2000).

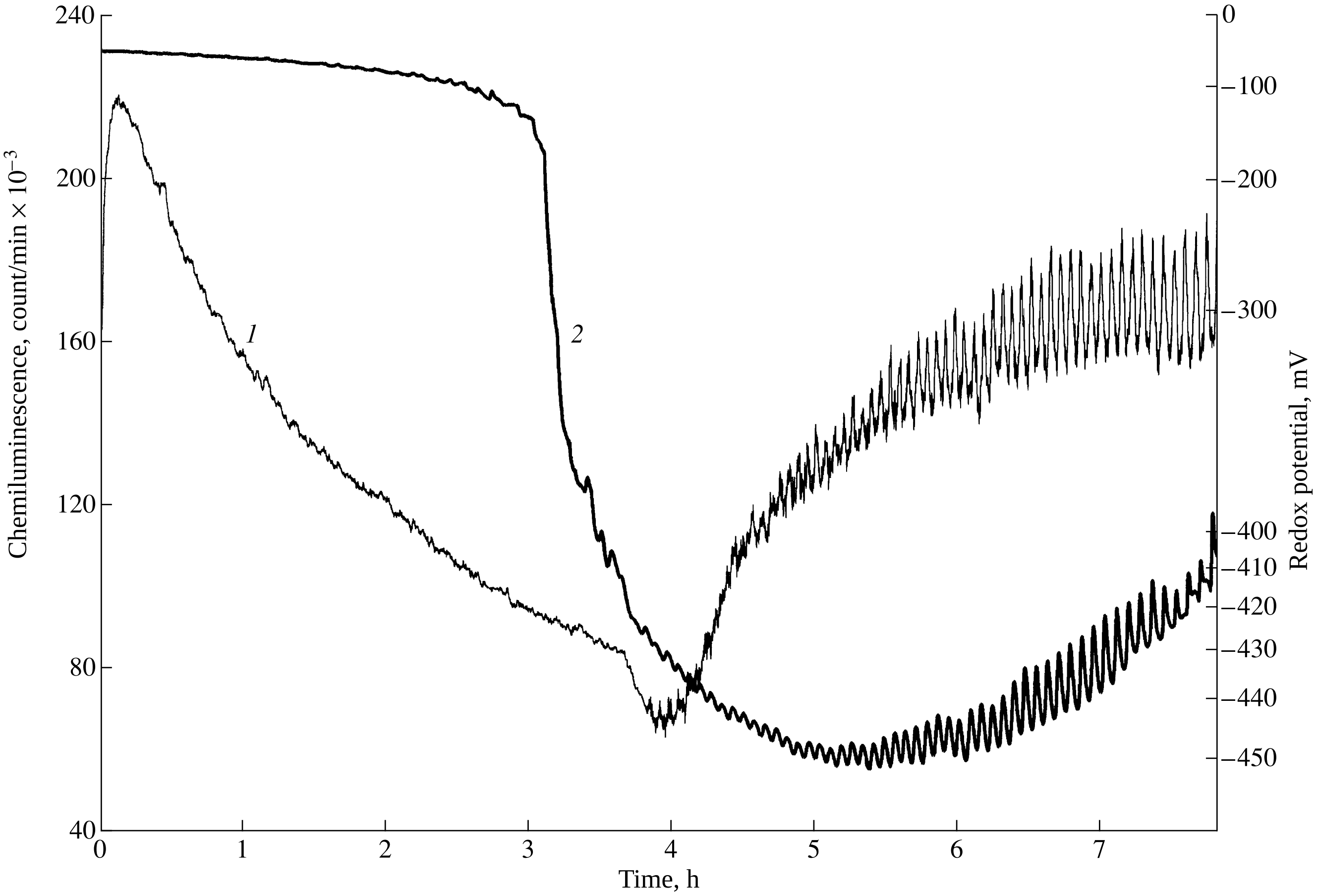

Fig. 1. Kinetics of (*1*) chemiluminescence development and (*2*) redox potential change in the methylglyoxal–ethanolamine system (concentrations are 10 and 30 mmol/l, respectively; pH 10.5) (the data were obtained during simultaneous measurements).

RESULTS AND DISCUSSION

Figure 1 shows the curves of the chemiluminescence and redox potential. As can be seen, oscillations are developed 3–5 h after mixing the reactants. By that time, all of the oxygen available in the solution is consumed (not shown in Fig. 1), and its diffusion from atmospheric air becomes the only source of oxygen. As a result, nonuniform luminescence over the vessel height is observed: most of emission belongs to near-surface layers (not shown). Figure 2 shows the fragments of chemiluminescence and redox potential curves at the stage of appearance of the oscillatory mode and the Fourier spectra of these time series. It is doubtless that both these parameters change consistently, and an almost exact correspondence of the frequency characteristics of oscillations is observed.

It should be mentioned that both periodic and aperiodic modes appeared in the system, and the spectral density in the Fourier spectra was concentrated in a region of 2–60 min. The duration and amplitude of oscillations depended on the composition and concentration of the starting reactants, pH, stirring, and surface area through which oxygen diffused into the system. For example, oscillations were detected only in alkaline solutions (at pH 9.5–12.0) at concentrations of methylglyoxal and amino compound of 5 mmol/l and higher. With an increase in the concentration of reactants, the duration of the oscillatory stage increased substantially, and the oscillations disappeared when the reaction system was stirred.

Thus, the following specific features characterize the new oscillatory system. First, both the chemiluminescence and redox potential oscillations are observed in the distributed system in which the specific rate of oxygen supply to the system is found. Second, transition metal ions in considerable concentrations are unnecessary (it is impossible to create conditions under which they are absent) for the appearance of the oscillations. Third, biologically important compounds (methylglyoxal and amino acids) directly participate in the oscillatory system. Moreover, the amino-carbonyl reaction occurs intensively in living organisms [10]. Taking into

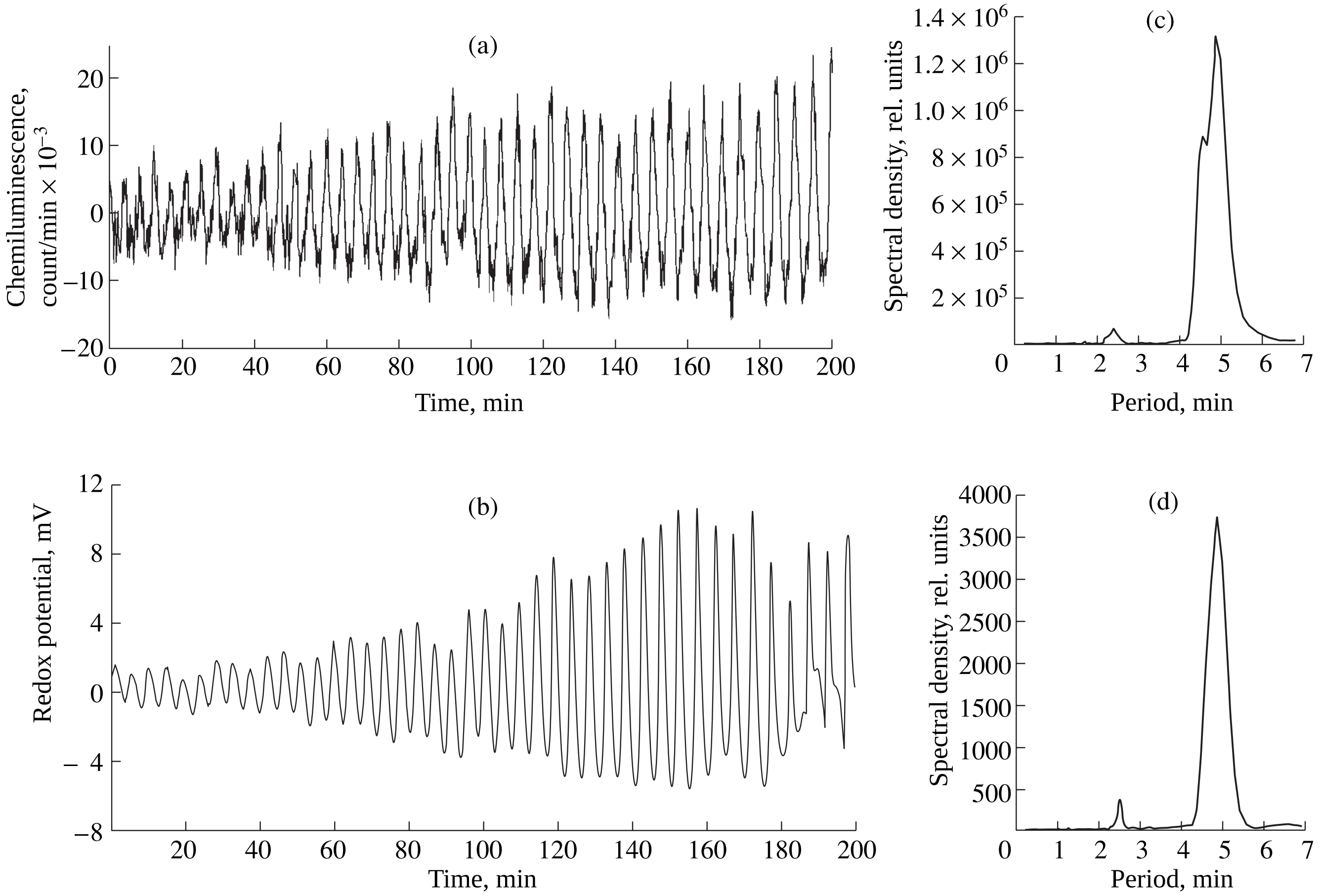

Fig. 2. Fragments of the (a) chemiluminescence development and (b) redox potential change at the stage of appearance of the oscillatory mode after the removal of (c, d) trends and the corresponding periodograms obtained by the Fourier analysis of the time series.

account these facts, we hope that the elucidation of the mechanism of the appearance of oscillations in the present system renovates the directions related to studying both oxidation reactions in an aqueous phase and complex dynamic properties inherent in biological systems.

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