React. Kinet. Catal. Lett., Vol. 34, No. 2, 249-254 (1987)

BROMINE HYDROLYSIS CONTROL AND TWO CONSECUTIVE OSCILLATORY DOMAINS IN CLOSED, CERIUM-CATALYZED GLYOXYLIC ACID BELOUSOV-ZHABOTINSKY SYSTEMS

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Received December 8, 1986
Accepted June 4, 1987

In closed, cerium-catalyzed glyoxylic acid Belousov-Zhabotinsky systems we found a new dynamic behavior, viz. the observation of two oscillatory regimes separated by a nonoscillatory region. Mechanisms for this intermediate nonoscillatory domain are discussed.

Наблюдали новое динамическое поведение системы Белоусова-Жаботинского для глиоксиловой кислоты, катализированной церием, заключающееся в двух колебательных режимах, разделенных неколебательным режимом. Обсуждаются механизмы для этих промежуточных неосцилирующих процессов.

INTRODUCTION

Kaner and Epstein [1] and Noszticzius and Bodiss [2] have recently reported about cerium-catalyzed glyoxylic acid oscillators. While these and other [3-4] authors assume that glyoxylic acid is a main intermediate in the malonic acid (MA) Belousov-Zhabotinsky (BZ) reaction [5] evidence has been found that glyoxylic acid is oxidized to formic acid under MA BZ conditions, while normally no formic acid is observed in this sys-

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tem [6]. This makes it doubtful that glyoxylic acid is a major intermediate in the malonic acid BZ reaction. Although the glyoxylic acid BZ oscillator seems now unrelated to the malonic acid oscillator, it is, besides the oxalic acid BZ reaction [7] one of the simplest catalyzed bromate oscillators and therefore of considerable interest.

In this paper we report a new dynamic behavior we have observed in closed, cerium-catalyzed glyoxylic acid BZ reactions, viz. the occurrence of two oscillatory regions separated by a nonoscillatory region. Similar behavior has been reported for a variety of other bromate oscillators [8-10] and a review has been given by Field [4].

EXPERIMENTAL

Experiments have been performed in a closed polarographic cell at 25 °C (± 0.1 °C) with a reaction volume of 25 cm^3. Oscillations were followed using a platinum electrode and a bromide ion selective electrode (Metrohm, Switzerland) against a Ag/AgCl double junction reference electrode (Metrohm). Potentials were monitored on a conventional two-channel x-t recorder. The reaction medium was stirred using a magnetic stirrer at approximately 500 rpm.

All chemicals were used without further purification and were, except for the glyoxylic acid, of analytical quality. Glyoxylic acids from two different suppliers were used (Sigma, USA and Merck, Darmstadt, FRG) and gave the same results. The purity of the glyoxylic acid was in both cases about 98 %. Oscillations were started by adding glyoxylic acid, $KBrO_3$ and $(NH_4)_2Ce(NO_3)_6$ to 25 cm^3 1 M H_2SO_4. Then the reactor was closed to the outer atmosphere and oscillations recorded.

RESULTS AND DISCUSSION

Figure 1 shows a typical run of the observed consecutive oscillatory domains of a closed, cerium-catalyzed glyoxylic acid BZ system. Under our experimental conditions, induction period lengths are generally very small and decrease with de-

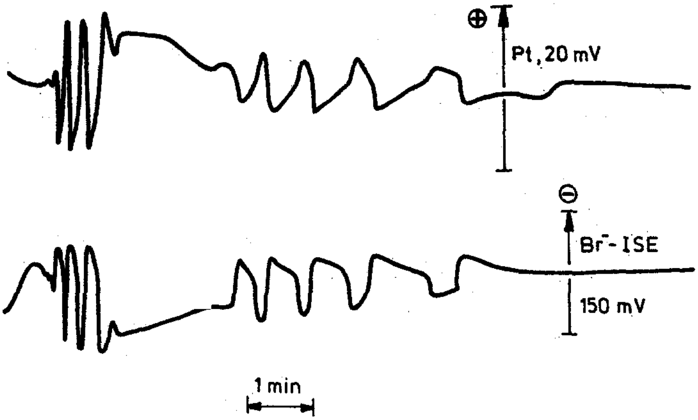

Fig. 1. Consecutive oscillations in the cerium-catalyzed glyoxylic acid BZ reaction, Initial concentrations: [glyoxylic acid]=0.3 M, [$KBrO_3$]=0.1 M, [Ce^{4+}]= = 2×10^{-3} M. Upper trace: oscillations observed at the platinum electrode, lower trace: oscillations observed at the Br^--sensitive electrode (Br^--ISE)

creasing initial cerium(IV) concentration. The amplitudes observed at the platinum electrode are small (about 20-40 mV) compared with the corresponding oscillations observed at the bromide ion selective electrode (which are in the range of 100-150 mV).

Figure 2 shows oscillations observed at the platinum electrode with two different initial cerium(IV) concentrations, viz. 2×10^{-3} M (curve A) and 6.5×10^{-3} M (curve B). We see that for the high initial cerium(IV) concentration (Fig. 2B) the induction period almost disappears and the nonoscillating period is somewhat lengthened.

After mixing of the reagents and during the oscillations we observe the production of elemental bromine and carbon dioxide.

Oscillations of the second oscillatory domain have generally greater period lengths and lower amplitudes. The nonoscil-

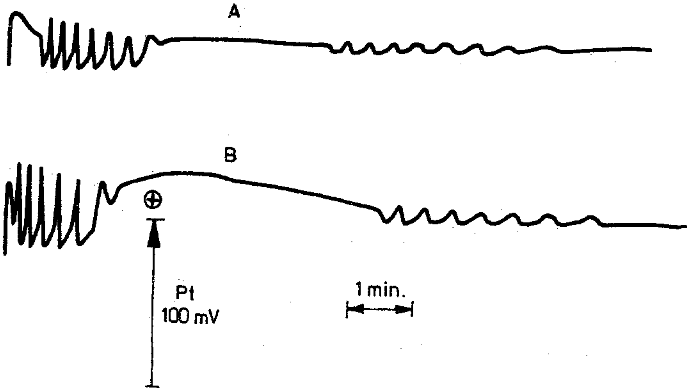

Fig. 2. Consecutive oscillations observed at the platinum electrode for two different initial cerium(IV) concentrations (A): 2×10^{-3} M and (B): 6.5×10^{-3} M. Other initial reagent concentrations: [glyoxylic acid] =0.15 M, $[KBrO_3]$=0.1 M

lating region which separates the two oscillatory domains is in an oxidized steady state and has the features of an induction period, i.e. the system is in a low bromide ion concentration state with a high cerium(IV) concentration. In this state a reaction analogous to reaction B of the Field-Kőrös-Noyes (FKN) mechanism [11] is the dominating process. When oscillations have stopped after the second oscillatory domain, the system is in a reduced steady state, i.e. the system has now a high bromide ion concentration and a low cerium(IV) concentration.

When nitrogen is rapidly bubbled through the system, no oscillations are observed and the reaction remains in an oxidized state. According to Field [12], this shows that the system is bromine hydrolysis controlled.

Noszticzius and Bodiss [2] noted that most of the glyoxylic acid is oxidized to CO_2, where oxalic acid might be a possible intermediate. If component process P2 is sufficiently slow, the consecutive oscillating regions could be explained by the two consecutive processes P1 and P2.

$$2HBrO_3 + 5CHO{\cdot}COOH \xrightarrow{Ce^{4+}/Ce^{3+}} 5(COOH)_2 + H_2O + Br_2 \quad (P1)$$

$$2HBrO_3 + 5(COOH)_2 \xrightarrow{Ce^{4+}/Ce^{3+}} 5CO_2 + 6H_2O + Br_2 \quad (P2)$$

That process P2 indeed can generate oscillatory behavior also in systems with no inert gas purging [7] has recently been demonstrated by Blume and Bader [13].

The appearance of the "quiescent" period separating the two oscillatory domains can, however, also be explained in the way that when carbon dioxide from process P2 becomes saturated in the aqueous phase, the resulting gas evolution withdraws bromine from the solution such that the system remains in an oxidized state with a low bromide ion concentration. Oscillations reappear again when bromine will – according to Henry's law – dissolve again (closed system!) and thus increase the bromide ion concentration due to bromine hydrolysis. We believe that this explanation also applies to a similar observation by Wittmann et al. [14] in the oxalic acid/acetone BZ reaction.

We do not think, however, that the intermediate nonoscillatory period is due to bromide ion inhibition. In that case the nonoscillatory domain should have been in a reduced state with a high bromide ion concentration.

A more detailed mechanistic study of our observed dynamics is being considered.

Acknowledgement. PR thanks the Norwegian Research Council NAVF for a travel grant to Budapest. EK thanks the soros Foundation for financial support.

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