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Organic Substrates Producing a Dual-Frequency Belousov-Zhabotinskii Oscillating Reaction

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Four organic substrates, acetoacetic acid methyl ester, 4-chloroacetoacetic acid ethyl ester, acetonedicarboxylic acid diethyl ester, and N-methylacetoacetamide, have been found to generate dual-frequency oscillations in the Belousov-Zhabotinskii type reaction system.

The most extensively investigated oscillatory chemical reactions are the Belousov-Zhabotinskii (BZ) type ones.1) In this reaction, organic substrate is oxidized by bromate ions in sulfuric acid medium in the presence of metal-ion catalyst. An acceptable detailed mechanism of temporal oscillations in BZ reaction with malonic acid has been worked out by Noyes and coworkers.2) The essential requirement regarding the organic substrate appears to be the presence of a reactive methylene group or a β-keto group.

Salter and Sheppard3) reported a dual-frequency oscillator with acetoacetic acid ethyl ester (AE, $CH_3COCH_2COOC_2H_5$) whose behavior is very similar to that of the normal malonic acid (MA, $CH_2(COOH)_2$) system except that a set of high-frequency, negatively damped oscillations in both the redox potential and the Br^- concentration is superimposed on the early part of the induction period. AE is only an example known until now as the substrate which produces a dual-frequency oscillator, but it has not been investigated in detail. In this paper, we report further results on the behavior of the dual-frequency BZ reaction.

All materials used were of the highest grade commercially available, and were used without further purification. The potentials of a platinum redox electrode and a bromide selective electrode against a mercurous sulfate reference electrode were continuously recorded. Experiments were performed in a thermally regulated glass container with a magnetic stirrer under the aerobic conditions at 20 °C, in almost experiments.

Dual-frequency oscillations have been obtained with the following substrates: acetoacetic acid methyl ester (AM, $CH_3COCH_2COOCH_3$), 4-chloroacetoacetic acid ethyl ester (CAE, $ClCH_2COCH_2COOC_2H_5$), acetonedicarboxylic acid diethyl ester (ADD, $CO(CH_2COOC_2H_5)_2$), and N-methylacetoacetamide (MAA, $CH_3COCH_2CONHCH_3$). Typical oscillatory responses of platinum electrodes obtained are shown in Fig. 1, where the oscillation in the case of AE is also illustrated for a compasison. The general shape of oscillations in the cases of the other substrates are similar to that of AE under the same conditions. But, the frequency, amplitude, and the total number of oscillations depend on the kind of the substrate.

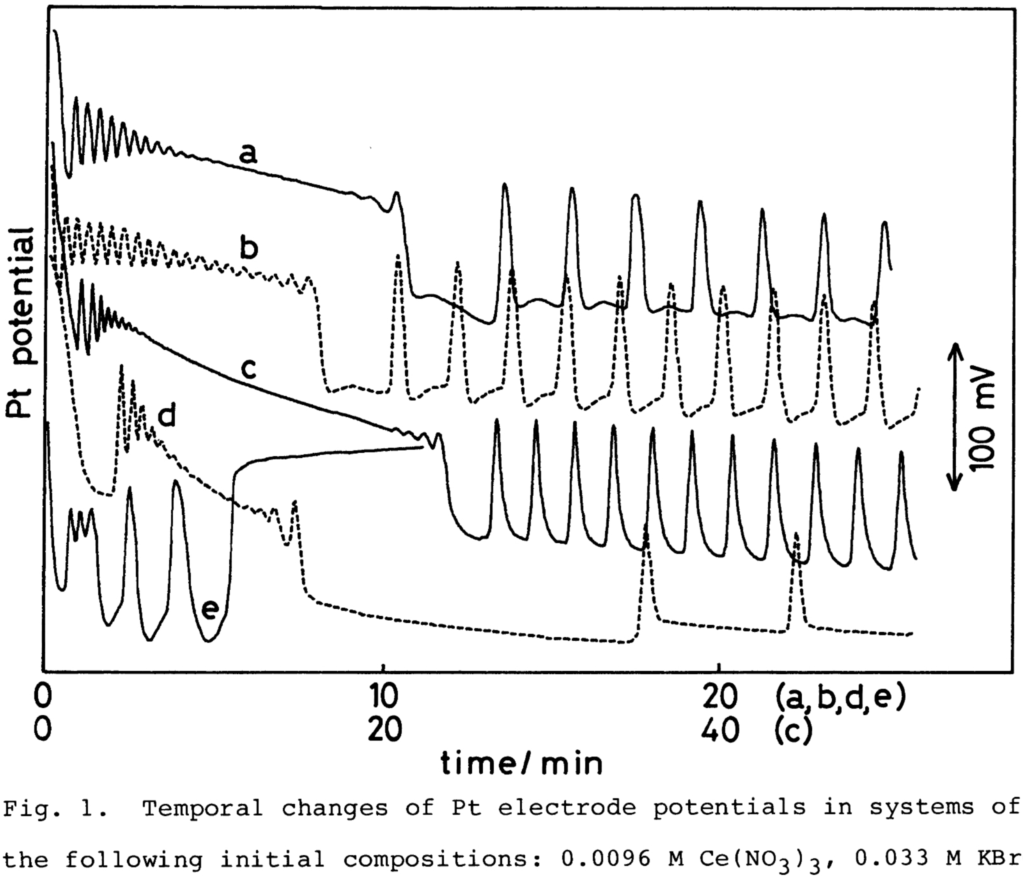

Fig. 1. Temporal changes of Pt electrode potentials in systems of the following initial compositions: 0.0096 M $Ce(NO_3)_3$, 0.033 M $KBrO_3$, 0.94 M H_2SO_4, and organic substrate (a: 0.077 M AE, b: 0.068 M AM, c: 0.039 M CAE, d: 0.018 M ADD, and e: 0.009 M MAA). 1 M = 1 mol dm^{-3}.

Dual-frequency oscillations were observed for the solutions containing a range of initial concentrations of components. We adopted the concentrations used in Fig. 1 as standard conditions. For the ADD system, the range of concentrations is shown in Table 1, where the concentration of one of the four components was varied while the concentrations of other three components were fixed at the standard conditions. The dependence of the periods of high- and low-frequency oscillations on temperature was investigated in the range of 25-35 °C for ADD. For both types of oscillations, log(1/period) is a linear function of inverse of temperature. The Arrhenius equation allows us to calculate two activation energies: 30 and 60 kJ/mol for high- and low-frequency oscillations, respectively, have been obtained.

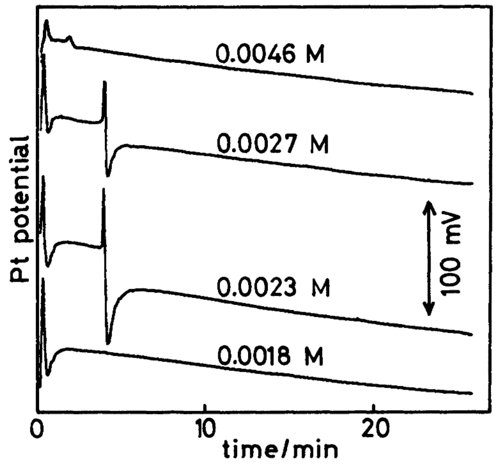

Fig. 2. Potential profiles of KG system.

Table 1. Conditions for the dual-frequency BZ reaction with ADD as organic substrate

Reactant	Concentration range/M
H_2SO_4	0.80 - 1.02
$KBrO_3$	0.027 - 0.034
$Ce(NO_3)_3$	0.004 - 0.012
ADD	0.015 - 0.025

Organic substrates capable of yielding dual-frequency oscillations shown in Fig. 1 are esters or acid amides of acetoacetic acid (or its derivatives). Since these organic species are hydrolyzed in acid medium, it would be considered that acetoacetic acid (or its derivatives), one of the hydrolysis products, produces the high- or low-frequency oscillations. It is difficult to check the influence of acetoacetic acid because of its unstability, but in the case of ADD substrate, β-ketoglutaric acid (KG, $CO(CH_2COOH)_2$) formed by hydrolysis is stabe, so that the effect of replacing ADD can be studied. The results are given in Fig. 2. It shows that ADD does not yield oscillations befitting to high- or low-frequency one. This means that the hydrolysis of the substrate is not a main factor for dual-frequency oscillations.

We have also found that the "pseudo-dual-frequency" oscillations appear with acetylacetone (AA, $CH_3COCH_2COCH_3$) or MA. In the AA substrate system (Fig. 3), the oscillation which arises initially damps after a while and then appears again. It seems that the potential profile does not consist of two oscillations, high- and low-frequency ones, but is simple oscillations posessing a "null period" during which the potential is nearly constant in the time course. In the case of the MA substrate system (Fig. 3), where the strong acid such as sulfuric acid is not added, the oscillation which arises initially suddenly shifts to the oscillation with a different frequency.

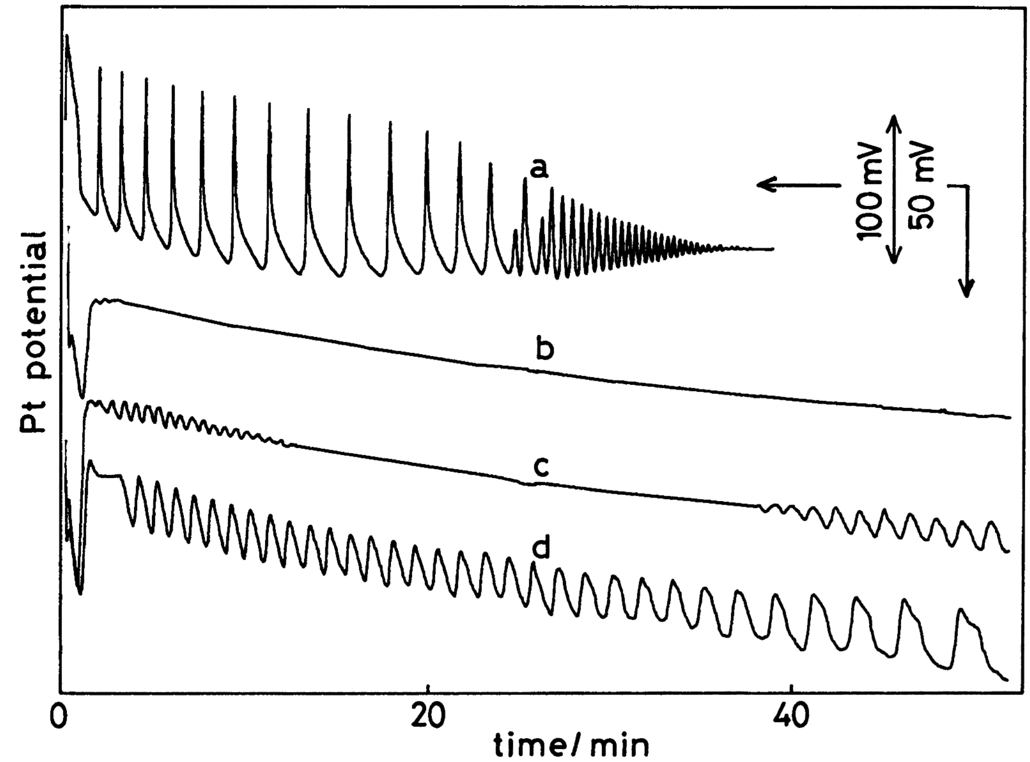

Fig. 3. Potential-time profiles. MA system (a): 2.01 M MA, 0.048 M $Ce(NO_3)_3$, and 0.451 M $KBrO_3$ at 30 °C. AA system: 0.020 M(b), 0.019 M(c), and 0.018 M(d) AA. Other components are in standard conditions.

Further detailed studies on the mechanism of dual-frequency oscillations are being considered.

References

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3) L. F. Salter and J. G. Sheppard, Inter. J. Chem. Kinet., 14, 815 (1982).

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