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Determination of thermodynamic parameters for enolization reaction of malonic and metylmalonic acids by using quartz crystal microbalance

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ABSTRACT

We investigated the process of a bromination reaction of malonic acid and methylmalonic acid in the Belousov-Zhabotinsky reaction by using a quartz crystal microbalance (QCM). The process involves an enolization reaction as a rate-determining step. We found that, in the step, the variation of Br_2 concentration induced an exactly quantitative shift of a resonant frequency of the QCM, based on the change of the surface mass on the QCM and the solution viscosity and density. This new finding enabled us to estimate the reaction rate constants and the thermodynamic parameters of the enolization reaction due to a QCM measurement. The values measured by the QCM were in good agreement with those measured by a UV-spectrophotometer. As a result, we succeeded to develop a new measurement method of a nonlinear chemical reaction.

1. Introduction

A quartz crystal microbalance (QCM) has been employed as a transducer of a surface mass and/or a solution viscosity and density into an electric signal [1–8]. This signal is measured as a resonant-frequency shift of a quartz crystal oscillation.

A small amount of mass deposited on the surface of the QCM leads to its resonant-frequency shift. In other words, a mass change of order of subnanogram can be detected by the measurement of the resonant-frequency shift. The relationship between the surface mass change, Δm, and the resonant-frequency shift of the QCM is described by the Sauerbrey equation [1]:

$$\Delta f_m = -\frac{2f_q^2}{A\sqrt{\rho_q \mu_q}}\Delta m \tag{1}$$

where Δf_m is the resonant-frequency shift due to Δm, f_q is the fundamental resonant frequency of quartz crystal, μ_q is the shear modulus of quartz crystal, ρ_q is the density of quartz crystal, A is the piezoelectrically active area. This property enables us to take advantage of the QCM as mass sensors of rigid materials [5,6].

On the other hand, to avoid in a liquid the large loss in a quality factor leading to instability and even cessation of oscillation, the QCM is operated with the one face in contact with a solution. For a Newtonian liquid, the equation derived by Kanazawa and Gordon predicts a linear relationship between the resonant-frequency shift and the square root of the density–viscosity product [2,3]:

$$\Delta f_\eta = -\frac{f_q^{3/2}}{\sqrt{\pi \rho_q \mu_q}}\sqrt{\rho_1 \eta_1} \tag{2}$$

where Δf_η is the resonant-frequency shift due to a solution viscosity and density, η_1 is the viscosity of a liquid, and ρ_1 is the density of a liquid. The relationship is applied to electrolytic solutions except for an intercept generated by deposition of electrolytes [9].

Therefore, when the QCM is used in an aqueous environment, both of a surface mass and a solution viscosity and density give rise to a resonant-frequency shift, ΔF, of the QCM [3–6]. That is, ΔF is given by

$$\Delta F = \Delta f_m + \Delta f_\eta \tag{3}$$

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The Belousov-Zhabotinsky (BZ) reaction is well-known as one of the most famous oscillating chemical reactions [10,11]. The BZ reaction exhibits a wide variety of nonlinear phenomena, e.g., multistability, periodicity, multiperiodicity or deterministic chaos.

Generally, nonlinear phenomena of the BZ reaction have been monitored by variation of redox potential or absorbance. In such situation, we have found that the oscillation of the BZ reaction was detected by ΔF [12,13].

In an initial reaction of the BZ reaction, bromomalonic acid is produced by bromination of malonic acid. In the reaction, a rate-determining step is an enolization reaction of malonic acid. The several papers have reported the rate constants and the thermodynamic parameters of the enolization reaction of malonic acid and its derivatives (methylmalonic acid and ethylmalonic acid). However, those were estimated only by conventional methods of a UV-spectrophotometer or a NMR [14–18]. Therefore, in this paper, we propose a new measurement method of the rate constants and the thermodynamic parameters by detection of ΔF of the QCM. Here, we used malonic acid and methylmalonic acid. This attempt shows a new field for the study of the chemical reaction with a nonlinear oscillation.

2. Experimental

2.1. Materials

Malonic acid (MA) (NAKARAI Tesque, Ltd., Japan), methylmalonic acid (MeMA), $NaBrO_3$, H_2SO_4, $FeSO_4 \cdot 7H_2O$, KBr (WAKO Pure Chemical Industries, Ltd., Japan) and O-phenanthroline$\cdot H_2O$ (DOJINDO, Japan) were of commercial analytical grade and were used without further purification. Water was purified by a Milli-Q apparatus (Millipore, Japan) and was deaerated before experiments. A bromine solution of 0.05 M (WAKO Pure Chemical Industries, Ltd., Japan) was also used for calibration curve.

2.2. QCM measurement

The schematic diagram of an experimental setup is illustrated in Fig. 1a. The enolization reaction was performed using 30 ml solution in a batch reactor (31 mm in diameter and 46 mm in depth). The batch reactor was covered with water jacket and the temperatures were controlled with accuracy of ±0.1 °C.

In order to monitor ΔF of the QCM due to the enolization reaction of MA and MeMA, a 9 MHz AT-cut QCM (SEIKO EG & G, Ltd., Japan) was employed. The QCM had the configuration of round of 8 mm diameter and a pair of the round platinum electrodes of 5 mm diameter (Fig. 1b). The QCM was connected to a series resonant TTL circuit (SEIKO EG&G QCA917-21, Japan), which caused the QCM to oscillate at the resonant frequency near 9 MHz. The TTL circuit was powered from a 5 V dc supply. ΔF was monitored by a universal frequency counter (Agilent technologies 53131A). The data was recorded in a PC with sampling time of 0.1 s.

In the present experiments, the one side of the QCM was sealed with a blank quartz crystal casing (Fig. 1b), maintaining it in an air environment, while the other side was contacted with a reaction solution. This casing is essential for the frequency stability of the QCM in an ionic solution. The one-face sealed QCM was vertically immersed into the reaction solution (Fig. 1a). The mixing levels of the solution were controlled using a stirrer bar (20 mm in length and 5 mm in diameter) and a magnetic stirrer. A stirring rate was kept constant at 300 rpm.

2.3. UV-spectrophotometer measurement

A shift of $[Br_2]$ was measured at $\lambda = 393$ nm by using a UV-spectrophotometer (Hitach High-Technologies U-1900, Japan). A reaction cell with an optical phat length of 1 cm was used. Temperatures were controlled with accuracy of ±0.2 °C and a stirring rate was kept constant at 300 rpm (6 mm in length and 1.5 mm in diameter). A sampling time was set at the range from 0.5 to 2 s depending on a whole measurement time. The solution system was the same as that of the QCM measurement.

3. Results and discussion

3.1. Chemical reaction

Bromination of MA occurs by way of the enolization reaction [15–18].

$$(COOH)-CH_2-(COOH)\ (\text{keto form}) \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (COOH)-CH = C(OH)_2\ (\text{enol form}) \qquad (R1)$$

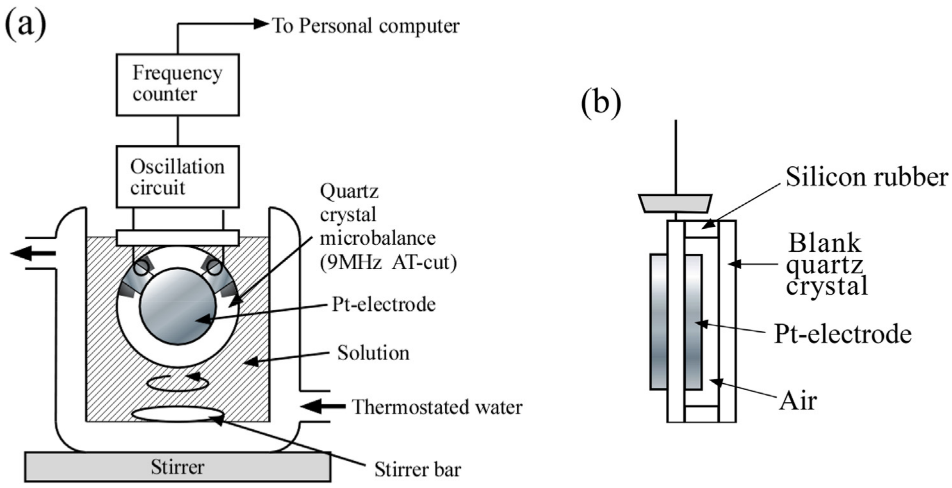

Fig. 1. (a) Schematic illustration of an experimental apparatus. (b) Schematic illustration of a one-face sealed quartz crystal microbalance.