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Thermal degradation of betanine in various water alcohol model systems

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Thermal degradation of betanine in the model systems water/glycerol, water/ethylene glycol and water/ethanol has been carried out at temperatures ranging from 60°C to 86°C. Water activity was chosen to be 0·87 and pH was adjusted to 5·0. The lowest stability of betanine and the lowest activation energy have been found for the system water/ethanol. This is in accordance with the idea of a nucleophilic attack on the structure $>N^+{=}CH-$ as the first step of the betanine degradation. It has been shown that the Guggenheim method is the most suitable for the treatment of experimental kinetic curves.

INTRODUCTION

The synthetic food colorants have been recently questioned owing to the harmfulness of some of them. Therefore extensive research has been carried out to replace them with natural pigments. The group of pigments found in red beet (*Beta vulgaris*) known as betalaines has been shown to be suitable as a red food colorant. The use of naturally occurring colours creates difficulties due to their low stability. For the major red pigment, betanine, several factors have been recognized to affect its stability: pH, temperature (Von Elbe *et al.*, 1974; Havlíkova & Míková, 1985; Saguy, 1979; Drdák & Vallová, 1990), oxygen (Saguy *et al.*, 1984), metal ions and light radiation (Aurstad & Dahle, 1973). The reaction order for the betanine degradation has been confirmed by several authors to be that of a first order reaction (Sapers & Horstein, 1979; Kearsley & Katsaboxakis, 1980; Drdák & Naščaková, 1984; Drdák *et al.*, 1990). In a recent study of Šimon *et al.* (1991) it has been shown that the rate of degradation depends on the nature of alcohol used for preparing the model systems and a mechanism of degradation has been assumed.

The purpose of this study is to follow the thermal degradation of betanine in various water/alcohol model systems at different temperatures and at a constant water activity.

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MATERIALS AND METHODS

Isolation of betanine

The red beet was washed, diced, pressed, pasteurized and fermented. In the fermentation, a strain of *Saccharomyces cerevisiae* sp., Badacsony 1, was used; fermentation took place at 26°C. The fermented red beet juice was centrifuged for 10 min at 3000 rpm and separated through a column packed with Sephadex G 25 using a 1% acetic acid solution as eluent. The fraction containing betanine was collected and concentrated at 40°C in a vacuum rotary evaporator.

Preparation of samples

The model systems water/glycerol water/ethylene glycol and water/ethanol have been chosen for this study, selecting the water activity value of about 0·87 which corresponds to the ratios (v/v) 60/40, 70/30 and 70/30 respectively. Betanine was dissolved in the model systems and the pH adjusted to 5·0 with NaOH. The concentration of betanine was 8·25 mg/litre. After having been flushed with nitrogen, the samples were thermostated at 60, 65, 68, 72, 75, 82 and 86°C. Absorbance was measured at constant intervals of time (Spekol 11, Carl Zeiss, Jena, Germany).

RESULTS AND DISCUSSION

The kinetic curves of absorbance, *A*, versus time were treated by two methods. The first, a classical method,

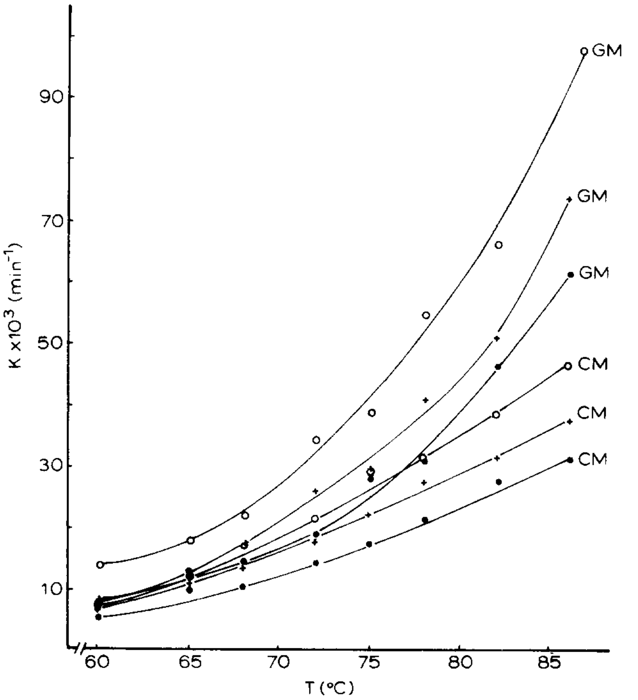

Fig. 1. Rate constants as a function of temperature. ●, Water/glycerol; +, water/ethylene glycol; ○, water/ethanol; CM, Classical method; GM, Guggenheim method.

consisted of obtaining the rate constants as the negative slopes of the dependences ln $A = f(t)$. However, these dependences are not perfect straight lines, but they are slightly convex curves. As has been shown recently (Šimon *et al.*, 1991), this can be explained by the light absorption of the products of betanine degradation. The systematic error caused by the presence of degradation products can be eliminated on treating the kinetic curves by the Guggenheim method which has been the other method used for the treatment of the experimental data.

The rate constants obtained by the classical and the Guggenheim methods are plotted in Fig. 1 as the dependences $k = f(T)$, where k represents the rate constant and T is temperature. As in previous work (Šimon *et al.*, 1991), due to the elimination of the systematic error, the Guggenheim rate constants are considerably higher than the classical ones. In the temperature range under study, the highest values of rate constants are found for the system water/ethanol. The constants for the system water/glycerol are slightly lower than for the system water/ethylene glycol. Hence, the lowest stability of betanine is observed in the system water/ethanol, which is more clearly demonstrated in Fig. 2 where the half-lives as a function of T are presented. The lowest stability of betanine in the ethanol/water system gives support to the idea that the first step of the betanine degradation is the nucleophilic attack on the $\rangle\overset{+}{N}{=}CH$— structure of betanine (Šimon *et al.*, 1991). Since ethanol has the highest electron density on the oxygen atom among alcohols studied in this work, it is the strongest nucleophilic agent and, consequently, betanine exhibits the lowest stability in the system water/ethanol.

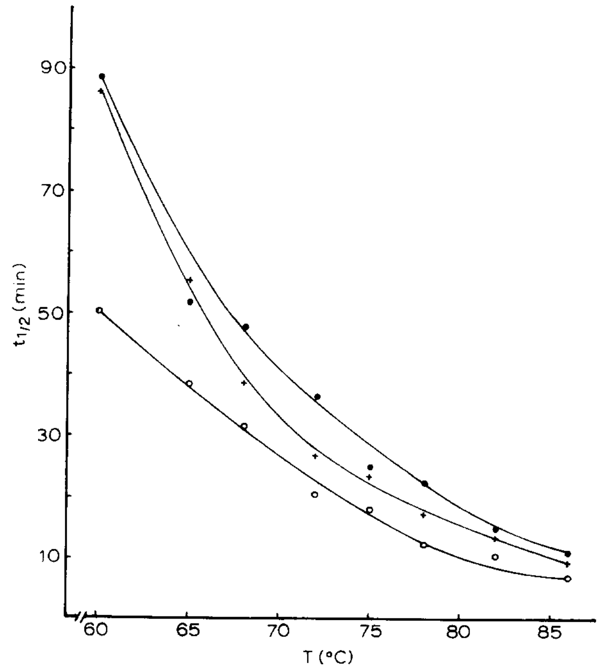

Fig. 2. Half-lives as a function of temperature. ●, Water/glycerol; +, water/ethylene glycol; ○, water/ethanol.

In Fig. 3, the dependences of ln k on $1/T$ are shown. The activation energies and preexponential factors calculated from these Arrhenius dependences are

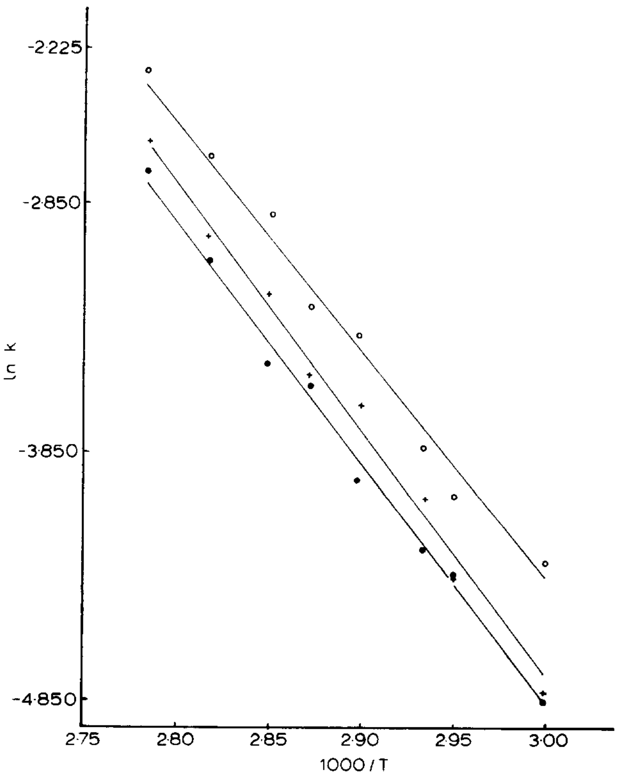

Fig. 3. Dependences of ln k on $1/T$ (T in K). ●, Water/glycerol; +, water/ethylene glycol; ○, water/ethanol.

Table 1. Activation parameters and correlation coefficients (ρ) for the betanine degradation in various water/alcohol systems

Alcohol	Guggenheim method			Classical method		
	log (A/min^{-1})	E_A (kJmol^{-1})	ρ	log (A/min^{-1})	E_A (kJmol^{-1})	ρ
Ethanol	10·06±0·49	76·3±3·3	−0·9945	8·40±0·59	66·6±3·9	−0·9898
Glycerol	10·05±0·48	77·5±3·2	−0·9950	8·03±0·46	65·4±3·0	−0·9936
Ethylene glycol	10·99±0·37	83·3±2·4	−0·9975	8·14±0·53	65·5±3·5	−0·9914

summarized in Table 1. The activation energies obtained by the Guggenheim method increase in the order ethanol → glycerol → ethylene glycol. The lowest activation energy for the system water/ethanol is in accordance with the fact that ethanol is the strongest nucleophilic agent; thus the activation energy for the nucleophilic attack on the $>\overset{+}{\mathrm{N}}{=}\mathrm{CH}-$ bond has the lowest value. The preexponential factors increase in the same order as the activation energies which is obviously due to the so-called compensation effect rather often encountered for the process in solutions (Laidler, 1965). Our results indicate that, in the study of betanine degradation in water/alcohol systems, the rate constants as well as the corresponding kinetic parameters vary for various alcohols used.

In Table 1, the kinetic parameters obtained from the classical rate constants are also listed. As can be seen, the kinetic parameters for both methods are quite different; the classical method leads to lower values than the Guggenheim one. The parameters obtained by the classical method are the same for the three systems studied, which does not enable us to recognize small differences among them. It is obvious that the systematic error in the determination of the rate constants by the classical method is transferred to the values of the kinetic parameters.

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