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Reactivity trends of the base hydrolysis of coumarin and thiocoumarin in binary aqueous–methanol mixtures at different temperatures

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Abstract

Rate constants for base hydrolysis of both coumarin and thiocoumarin have been studied in different binary aqueous–methanol mixtures at temperature range from 288 to 313 K. The activation parameters of the reactions were evaluated. Moreover, the change in the activation barrier of the investigated compounds from water to water–methanol mixtures were estimated from the kinetic data.

Keywords: Coumarin; Thiocoumarin; Activation barrier; Base hydrolysis; Rate

1. Introduction

The general chemical structure of coumarins consists of a benzene moiety fused to a-pyrone rings, and they are a class of phenolic substances commonly found in plants. Coumarin is the parent organic compound of a class of naturally occurring photochemicals found in many plant species such as meliot, tonca beans, lavender, sweet clover grass and licorice. It occurs in food plants such as strawberries, apricots, cherries, and cinnamon. It is thought to work as a pesticide for the plants that produce it.

This oxygen heterocycle is best known for its fragrance, described as a vanilla-like odor or the aroma of freshly mowed hay. Coumarin has been identified in the 1820s, but synthesized in the laboratory since 1868 and used to make perfumes and flavorings. It is the odoriferous principle of wood ruff which led to its wide-spread use as a perfumery chemical in industry [1]. Coumarin derivatives have also found applications as fluorescent dyes [2], antitumor agents [3], antifungals [4], anticoagulants [5], antibacterials [6] and insecticides [7], proliferators of HIV [8,9] and particular human malignant cell lines in vitro [10,11], as well as affecting tumor activity against several in vivo tumor types [12–14].

The chemistry of thiocumarin has mostly been neglected compared to that of coumarins and related systems [15]. Thiocoumarins are very important compounds due to their numerous pharmaceutical uses. Some of these compounds have been reported to act as nervous system depressants [16], antibacterial agent [17] and as building blocks for the synthesis of condensed and spiro coumarins [18].

Solvent effects on reactivity trends have been investigated for a variety of organic and inorganic reactions [19]. However, the extent of the interaction of the solvent environments of the initial and transition states with the solvent co-sphere of an added substance [20] should be considered to understand solvent effects on the reaction rate. Moreover, analysis of solvent effects on reactivities in terms of contributions from the initial and transition states can lead to full explanations of these trends [21].

In continuation of the previous work on chromone, coumarins and thiocoumarin [22–24] and to gain more information about the activation parameters of the base hydrolysis of coumarin and thiocoumarin, we report here the effects of methanol as co-organic solvent on the kinetics of the base hydrolysis of coumarin and thiocoumarin.

2. Experimental

All materials, sodium hydroxide, sodium chloride, coumarin, thiocoumarin and methanol (MeOH) used in this study were the

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purest commercially available materials. The stock solutions of NaOH and NaCl were prepared by dissolving the calculated amounts of AnalaR samples in redistilled water.

Kinetic measurements were carried out spectrophotometrically by following the absorbance with time at λ_{max} corresponding to the absorption maximum of each compound (coumarin, 285 nm; thiocoumarin, 370 nm) over at least three half-lives. Pseudo first-order conditions were applied, by mixing multifold greater concentration of NaOH than that of the compound. The total ionic strength of the reaction mixture was kept constant at 0.1 M by using NaCl. The kinetic data were monitored by using JASCO model V530 spectrophotometer and the desired temperature was controlled by Haake F3-K ultrathermostat.

The activation parameters of the mentioned reactions were calculated by least squares of Arrhenius and Eyring plots. In this approach we discuss the initial state–transition state analyses of solvent effects on reactivities of these compounds. The change in the activation barrier ($\delta_m \Delta G^{\#}$) values for coumarin and thiocoumarin when transferred from water to various (v/v) ratios of water–MeOH mixtures at different temperatures were figured out.

3. Results and discussion

It can be inferred from the repeated spectra scan (cf. Fig. 1) that the base hydrolysis of coumarin and thiocoumarin by NaOH takes place in one stage and leads to the rate determining opening of the pyrone ring and the formation of a salt of coumaronic and thiocoumaronic acids [25] as shown in the following scheme:

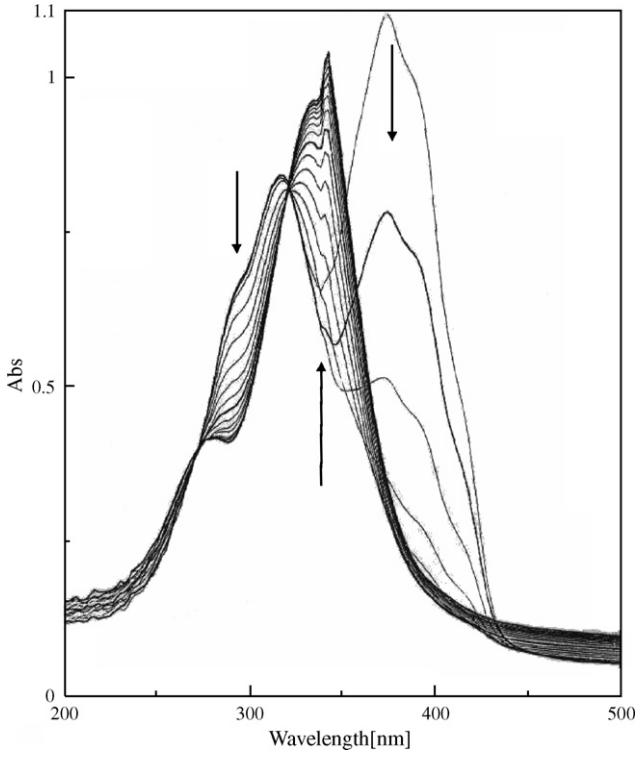
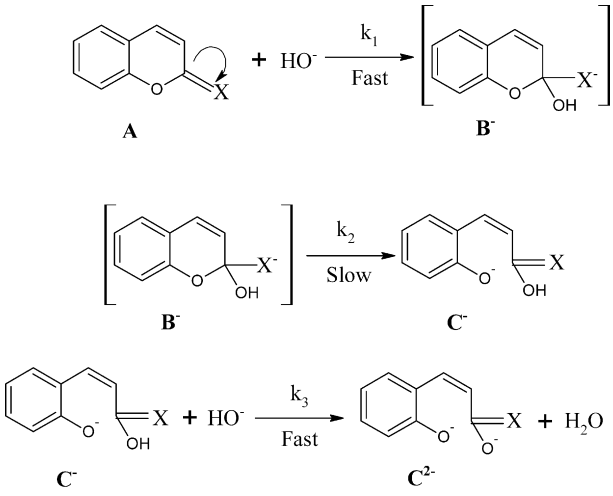


Fig. 1. Repeated spectral scan of the base hydrolysis of thiocoumarin at 298 K.



X = O , Coumarin
X = S , Thiocoumarin

The observed first-order rate constants (k_{obs}) as a function of [OH^-] and in the presence of different water–MeOH ratios at different temperatures are reported in Tables 1 and 2.

The dependence of k_{obs} on base concentration is linear for coumarin and thiocoumarin, without significant intercept (cf. Figs. 2 and 3). Hence the base hydrolysis reaction follows the

Table 1
The observed first-order rate constant (10^3 k_{obs}, s^{-1}) values[a] for the base hydrolysis of coumarin in various ratios (v/v) of MeOH in the presence of different [NaOH] and different temperature at $I = 0.1$ M

Temperature (K)	[NaOH] (M)	MeOH%			
		0	20	40	60
288	0.005	0.94	0.70	0.30	
	0.01	2.03	1.35	0.51	
	0.02	4.19	3.10	1.07	
	0.03	6.83	4.20	1.82	
293	0.005	1.63	1.05	0.43	0.16
	0.01	3.21	2.00	0.82	0.30
	0.02	6.40	4.21	1.86	0.81
	0.03	8.87	6.15	2.84	1.01
298	0.005	2.08	1.12	0.50	0.19
	0.01	4.31	2.52	0.98	0.36
	0.02	9.15	5.22	2.10	0.95
	0.03	13.20	8.03	3.35	1.44
303	0.005	3.12	1.85	1.00	0.41
	0.01	6.32	3.81	2.02	0.80
	0.02	12.01	8.09	4.15	1.63
	0.03	17.50	11.95	6.08	2.30
308	0.005	5.13		1.40	0.52
	0.01	9.12		2.60	1.25
	0.02	19.00		5.40	2.20
	0.03	26.05		8.00	3.22
313	0.005		4.00		0.97
	0.01		7.92		1.80
	0.02		15.75		3.21
	0.03		23.60		5.02

[a] Maximum error is 2%.