

REACTIVITY COMPARISON OF DI- AND MONOCHLOROTRIAZINYL DYES WITH METHANOL IN SUPERCRITICAL CO₂

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In a previous research of a dichlorotriazinyl dye, it was observed that supercritical carbon dioxide positively influence the reaction with methanol at 393 K, of the first reaction product, which is a monochlorotriazinyl compound. In order to know if that increase was not an isolated effect, larger temperature range was studied for the methanolysis reaction in pure methanol and in supercritical carbon dioxide. Reactions are carried out in a high-pressure batch reactor at 333, 353 and 373 K and 300 bar, when supercritical carbon dioxide was the reaction solvent. It has been found that rate constant values of k_2 , which determines the reactivity of monochlorotriazinyl dye, were the largest in supercritical carbon dioxide up to a factor 20 compare to pure methanol. Moreover, the lowest activation energy was also found for k_2 in supercritical carbon dioxide with a value of $50 \pm 13 \text{ KJmol}^{-1}$.

INTRODUCTION

In the conventional aqueous textile dyeing process large amounts of water are used causing ecological and economical problems due to the wastewater treatment. In consequence, during the last 20 years different research groups [1,2] has been developed a water-free textile dyeing process. Supercritical carbon dioxide is proposed as dye solvent instead of water for environmental, economical and chemical reasons. Its high diffusion rates and low mass transfer resistance facilitates the penetration of the dye into the fiber. Moreover, reaction rates increase in supercritical carbon dioxide over those observed in aqueous medium [3].

Dyeing cotton in supercritical carbon has not been possible yet using reactive dyes. These dyes react with cotton forming a covalent binding and improving the fixation of the dye with the textile. Study the reaction kinetics of the reactive dyes, has been done by different authors, [4,5] as an essential step for the optimization of the dyeing process of cotton. In the kinetics studies the cotton is substituted by methanol, therefore, reactions in homogeneous conditions can be done isolated from other dyeing factors as, affinity of the dye for cotton or solubility of the dye in supercritical carbon dioxide.

In a previous research the reaction kinetics with methanol of a dichlorotriazinyl dye has been studied [6]. In that research, an increase on the second rate constants was observed in supercritical carbon dioxide at 393 K.

In this work the reaction kinetics of a dichlorotriazinyl dye is investigated at different temperatures to estimate, if in supercritical carbon dioxide the increase of the second rate constant, which determines the reactivity of monochlorotriazinyl dye, was not an isolated effect. The reactions are carried out for pure methanol at 333, 353 and 373 K and for supercritical carbon dioxide, at the same temperatures and 300 bar.

MATERIALS AND METHODS

I. Materials

The dichlorotriazinyl dye used in this study was synthesized for a well-known dye manufacturer of reactive dyes. The carbon dioxide from Hoek Loos exhibited a purity of 99.97%. The methanol and acetonitrile used were HPLC grade from Rathburn and Acros respectively

II. Experimental set-up and Procedure

A high-pressure batch reactor was used to carry out experiments in supercritical conditions. The reactor designed for operating up to 350 bar, consists of a 150 mL pressure vessel connected to a pressure manometer and a needle valve.

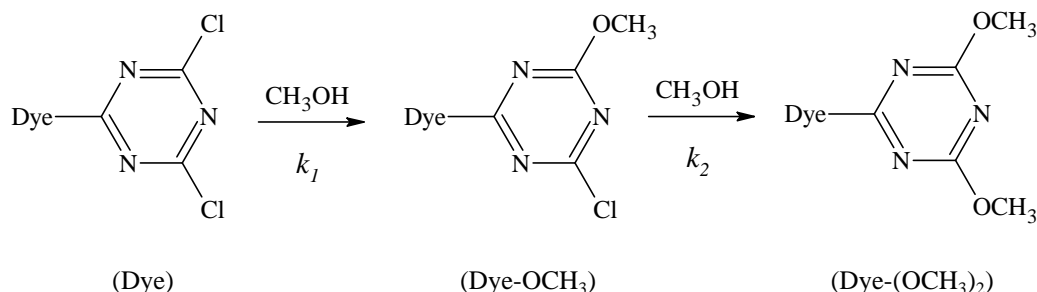
To carry out the kinetics experiments a suspension of 0.001 g of the dye in 50 mL of methanol was made and placed in an ultrasonic bath for 5 min to complete the dissolution of the dye. For the reactions in supercritical carbon dioxide, 1 mL of the dye solution in methanol was poured into the reactor. Then to reach 300 bar for each temperature, a weighed amount of liquid carbon dioxide was added to the reactor via the valve from a CO₂ gas cylinder. For the reactions of the dye in pure methanol, 25 mL of the dye solution described above were poured into the reactor. In both experimental procedures the reactor was placed in a thermostatic bad at 333, 353 and 373 K. After a sufficient reaction time, the reaction was stopped by cooling and a sample was very carefully taken from the reaction mixture by opening the valve. The sample was immediately analyzed by HPLC.

III. HPLC analyses

The chromatographic analyses were performed with a Chrompack liquid chromatograph with an (250×4.6 mm) Inertsil 5 ODS-2 column and using (85:15) (v/v) acetonitrile and water as mobile phase at a flow rate of 1 mL/min. Samples of 20 µL were injected with a Marathon autosampler and the chromatographic column was maintained at 298 K. The dye samples were detected at the maximum absorption wavelength (513 nm) with a Varian ProStart 310 UV/VIS Detector.

RESULTS AND DISCUSSION

A consecutive bimolecular nucleophilic substitution occurs when dichlorotriazinyl dyes reacts with nucleophiles, like methanol. [7]. The reaction of the dye with methanol can be schematically written as follow.



In our previous research it was observed that the methanolysis reaction of the dichlorotriazinyl dye followed a pseudo-first order kinetics in pure methanol and in supercritical carbon dioxide. This kinetics is observed when one of the reactants is present in large excess. The concentrations of dye, methanol and carbon dioxide were chosen in our experiments to conform such kinetics.

A first-order kinetic model for consecutive reactions was used to predict the dye concentrations during the reaction using the rate constant values experimentally determined. The kinetic model is described by the following equations [8].

$$[Dye]_t = [Dye]_0 \exp(-k_1 t) \quad (1)$$

$$[Dye - OCH_3]_t = [Dye - OCH_3]_0 \exp(-k_2 t) + \frac{k_1 [Dye]_0}{k_2 - k_1} (\exp(-k_1 t) - \exp(-k_2 t)) \quad (2)$$

$$[Dye - (OCH_3)_2]_t = [Dye]_0 - [Dye - OCH_3]_t - [Dye]_t \quad (3)$$

In equation (2), the term, $[Dye - OCH_3]_0 \exp(-k_2 t)$, can be omitted since no reaction has taken place at time 0 min.

After a certain reaction time, the concentrations of dye and reaction products, Dye-OCH₃ and Dye-(OCH₃)₂, were determined by HPLC analysis. The peak areas of the components were analyzed at their wavelength of maximum absorption; due to the Lambert-Beer law, these are linearly related to their concentrations. Therefore, the concentrations of the dye and reaction products can be replaced by the HPLC peak areas.

From this study the reactivity of dichlorotriazinyl and monochlorotriazinyl dyes, which is the first reaction product (Dye-OCH₃), can be compared. Determining the rate constants, k_1 and k_2 , an overview of the reactivity of the two types of dye with methanol, in pure methanol and supercritical carbon dioxide as reaction solvents, can be obtained.

As it is expected, an increase of k_1 and k_2 with temperature was found. This can be observed in the Arrhenius plots from figure 1 (a) and (b).

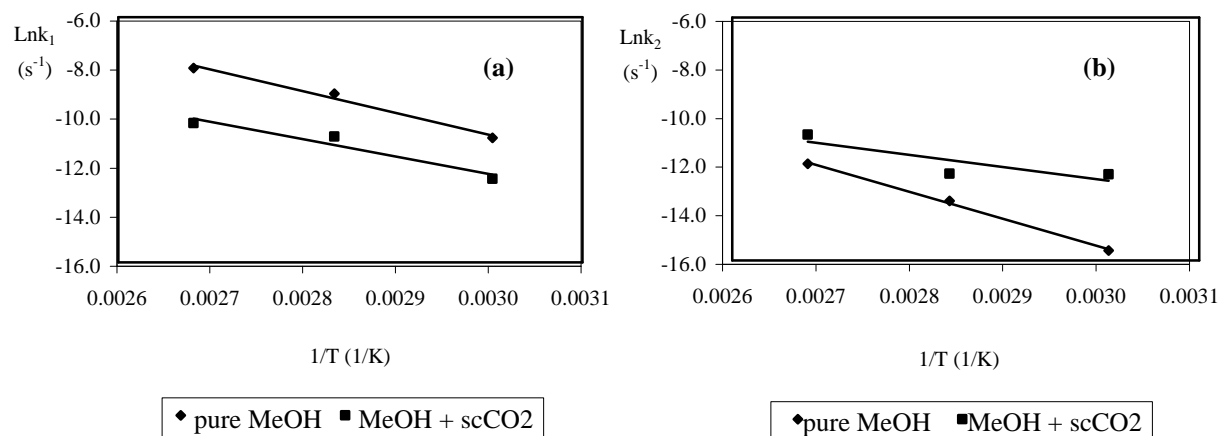


Fig 1. Arrhenius plot of k_1 (a) and k_2 (b) in supercritical carbon dioxide and pure methanol at different temperatures

To obtain the best values for k_1 and k_2 , the least square method was used to minimize the difference between the experimental data and the data predicted by the model. The rate constants values are shown in the following table.

Table 1. Values of the rate constants k_1 and k_2 at different temperatures in pure methanol (pure MeOH) and supercritical carbon dioxide (scCO₂).

T(K)	k_1 (10^{-5} s^{-1})		k_2 (10^{-5} s^{-1})	
	pure MeOH	scCO ₂	pure MeOH	scCO ₂
333	1.8	0.3	0.02	0.4
353	11	1.9	0.1	0.4
373	31	3.3	0.6	2.0

Rate constant k_1 shows the largest values in pure methanol and in supercritical carbon dioxide, except at 333 K where is a factor 1.3 larger in supercritical carbon dioxide.

Contrary to k_1 , k_2 has the largest values for the reactions in supercritical carbon dioxide for all temperatures up to a factor 20. This confirms that large values of k_2 in supercritical carbon dioxide was not an isolated effect observed in a previous research.

These results indicate that a monochlorotriazinyl dye, which is the first reaction product (Dye-OCH₃) from the methanolysis reaction of our dichlorotriazinyl dyes, can be more suitable dye to react with methanol in supercritical carbon dioxide.

The activation energy for k_1 and k_2 in pure methanol and in supercritical carbon dioxide were calculated from the Arrhenius plots, figure 1(a) and (b). These values are shown in the table 2.

Table 2. Activation energy for k_1 and k_2 in pure methanol (pure MeOH) and supercritical carbon dioxide (scCO₂), over the range of temperature (333K – 373K). Their standard deviations are also showed.

	Activation Energy (kJ mol ⁻¹)	
	pure MeOH	ScCO ₂
k_1	60 ± 10	61 ± 7
k_2	74 ± 11	50 ± 13

The activation energies of k_1 are practically equal independently of the reaction solvent. However for k_2 , the lowest activation energy is observed in supercritical carbon dioxide. This value is also lower than those observed in pure methanol.

Even if the largest rate constant values were obtained for k_1 . It is k_2 in supercritical carbon dioxide, which has the largest values compare to pure methanol. In addition, the lowest activation energy value was also observed for k_2 in supercritical carbon dioxide.

It seems that supercritical carbon dioxide is an excellent reaction medium, which favoured the nucleophilic attack of methanol to the monochlorotriazinyl dye form.

CONCLUSIONS

From the kinetics studies it has been found that k_1 and k_2 increase with temperature independently of the reaction solvent

k_1 showed the largest values in pure methanol, except at 333K where a factor 1.3 larger in supercritical carbon dioxide was measured. Contrary to k_1 , k_2 had the largest values in supercritical carbon dioxide up to a factor 20 for all temperatures.

The activation energies for k_1 were 60 ± 10 and 61 ± 7, in pure methanol and supercritical carbon dioxide respectively. For k_2 , a value of 74 ± 11 was found in pure methanol while for supercritical carbon dioxide the lowest value, 50 ± 13, was found.

Monochlorotriazinyl dyes might be more suitable dyes for reaction with nucleophiles in supercritical carbon dioxide. However, it cannot be assumed that the same reactivity will be observed with cotton, since more research is needed on the substantivity of the dyes for cotton or solubility of the dyes in supercritical carbon dioxide.

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