

Scientific paper

The Basic Hydrolysis of Malachite Green in β -Cyclodextrin/Cetyltrimethylammonium Bromide (CTAB) Mixed System

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Abstract

The basic hydrolysis of malachite green (MG) was studied in the mixed systems of β -cyclodextrin (β -CD) and cetyltrimethylammonium bromide (CTAB) at 25 °C. The observed rate constant, (k_{obs}) increases with increase in concentration of β -CD until saturation is reached while at constant β -CD concentration it varies with CTAB concentration in a sigmoid shape curve which is analogous to positive cooperativity in enzymatic reaction. The kinetic analysis shows that the major effect of CD on the system is the complexation of the surfactant monomers which delays the formation of micelles. The data obtained fit the pseudophase model of micellar reaction.

Keywords: Basic hydrolysis; malachite green; micellar pseudophases

1. Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides consisting of six, seven or eight α -D-glucose units and are respectively called α -, β -, and γ -cyclodextrins. They are produced by enzymatic degradation of starch followed by elaborate purification process. These systems possess a toroidal or hollow, interior and hydrophilic rims formed by primary and secondary OH groups. By virtue of their unusual shape, CDs can incorporate within their cavities molecules of the correct fit and hydrophobicity in solution or in solid form.^{1,2} The beneficial modification of guest molecular properties after the formation of the inclusion compounds leads to large number of applications related to chemical synthesis and catalysis, pharmaceutical chemistry and analytical chemistry.^{3–6} Surfactants are particularly strongly complexed by β -cyclodextrin, with the hydrophobic hydrocarbon chain tail usually enfolded within the cavity. This complex formation increases the concentration of surfactant required for micellization.^{7,8}

In this work, we study the basic hydrolysis of malachite green in β -cyclodextrin/cetyltrimethylammonium bromide mixed system. This alkaline fading of malachite green has been used many times for studies in normal mi-

celles, micelles in the presence of additives, reverse micelles and clusters and it has become a useful probe for studying chemical reactivity in organized media.⁹

Only very few works have been reported on the effect of β -cyclodextrin/surfactant mixed system on chemical reactions. In the basic hydrolysis of N-methyl-N-nitroso-p-toluenesulfonamide (MNTS) in mixed β -cyclodextrin/tetradecyltrimethylammonium bromide (TTBr) surfactant systems,¹⁰ there is an increase in the rate constant because TTBr complexation by β -CD expels MNTS in the bulk aqueous medium where the reaction is faster. However there is a decrease in the rate constant in the basic hydrolysis of nitrophenyl acetates (NPA) in β -CD/TTBr.¹¹ In hydrolysis of crystal violet (CV) in mixed β -cyclodextrin/CTACl surfactant systems, there was no catalytic effect below the critical micelle concentration of the surfactant which is different from that of MNTS and NPA.¹²

In this present work the basic hydrolysis of malachite green in β -CD/CTABr mixed system, one would expect similar behaviour to that observed in basic hydrolysis of CV in that both crystal violet (CV) and malachite green (MG) are members of the same triphenylmethane dye family.

2. Experimental

2.1. Materials

Malachite green (MG) was obtained from Bektoh (Germany) was used without further purification. It was characterized by its visible spectrum, which gave a molar extinction coefficient of $147,988 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ in agreement with the literature values at λ_{max} of 618 nm.¹³ The β -CD and hexadecyltrimethylammonium bromide (CTAB) were obtained with the highest available purity from Fluka and used as received. The purity of the surfactant (CTAB) was verified by determining its critical micelle concentration as described in our previous work.¹⁴ Sodium hydroxide was purchased from Merck. All solutions were prepared in glass distilled water.

2.2. Kinetics

The measurement of kinetic data of the base hydrolysis of malachite green were established by monitoring the decrease in absorbance of the dye at absorption maximum λ_{max} as function of time using a α -Helios Pye-unicam spectrophotometer fitted with an automatic cell changer and thermostable cell compartments.

The reaction components were calculated and mixed in a 1 cm (3 cm^3) quartz cell, with the dye being added last to ensure minimum pre-mixing reaction. All experiments were carried at $25.0 \pm 0.1 \text{ }^\circ\text{C}$. The concentration of the dye was maintained at $5.77 \times 10^{-5} \text{ mol dm}^{-3}$ (0.2 absorbance) in order to avoid complication that may arise from dependence of the hydrolysis on concentration of the dye. The concentration of dye was much lower than that of sodium hydroxide. The sodium hydroxide concentration was maintained constant at $0.001 \text{ mol dm}^{-3}$ for all the reactions. The concentrations of β -CD varies from 0 to $0.005 \text{ mol dm}^{-3}$ while the choice of surfactant concentrations was based on the structure in the $k_{\text{obs}} - [\text{CTAB}]$ profile, usually from zero to much above the critical micelle concentration (c.mc.). All runs were performed under pseudo first order kinetics. The observed rate constants were obtained from the slope of $\ln(A_t - A_\infty)$ versus time where A_t and A_∞ are the absorbance at a given time (t) and at infinity time respectively. The reaction proceeded to completion as judge from the complete fading of the dye at the end of the reaction. The values of the pseudo-first order rate constants were reproducible.

3. Result and Discussion

3.1. Effect of CD on the Basic Hydrolysis of Malachite Green

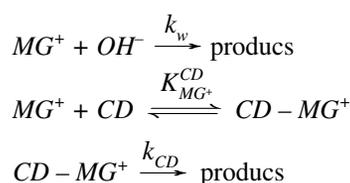
The alkaline of fading of stable triarylcarbocations is a reaction with a long chemical tradition which has become useful for studying chemical reactivity in organized

media.⁹ The reaction can be represented as



The basic hydrolysis of MG in the presence of β -CD was studied. The overall data at constant hydroxide ion concentration of $0.001 \text{ mol dm}^{-3}$ and varying the [CD] in the range of 0– $0.0045 \text{ mol dm}^{-3}$ show that the hydrolysis is catalyzed by addition of CD. Fig. 1 shows a plot of k_{obs} vs [CD] at $25 \text{ }^\circ\text{C}$. The plot shows saturation at [CD] greater than $0.0010 \text{ mol dm}^{-3}$.

The catalysis is as a result of the possibility of nucleophilic attack by an ionized hydroxyl group on the MG^+ associated with the CD which has been reported in the literature.¹² The variation of the rate constant (k_{obs}) with CD is treated on the assumption that the reactions occur as shown in scheme 1:



where k_w is the rate constant in bulk water phase, k_{CD} is the catalytic rate constant of CD and $K_{\text{MG}^+}^{\text{CD}}$ is the binding constant of MG^+ to the CD. This binding constant is given by the following equation

$$K_{\text{MG}^+}^{\text{CD}} = \frac{[\text{CD} - \text{MG}^+]}{[\text{CD}][\text{MG}^+]} \quad (2)$$

This model leads to the following relationship for this reaction as previously reported.¹²

$$k_{\text{obs}} = \frac{k_w[\text{OH}^-] + k_{\text{CD}}K_{\text{MG}^+}^{\text{CD}}[\text{CD}]}{1 + K_{\text{MG}^+}^{\text{CD}}[\text{CD}]} \quad (3)$$

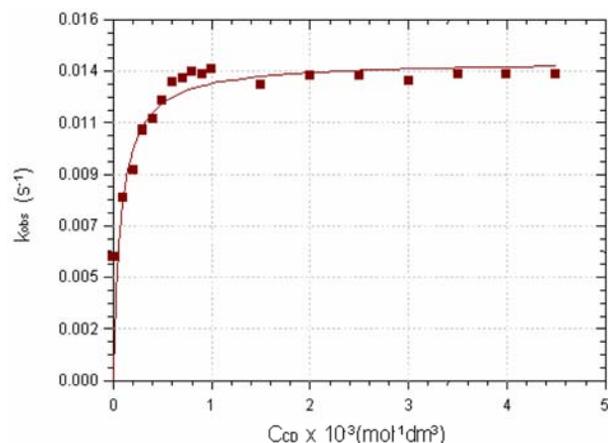


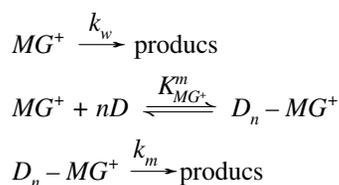
Figure 1: The effect of CD on the observed rate constant (k_{obs}). The unbroken line is the theoretical value from the curve fitting of the model

Using MicroMath Scientist for windows software to fit the data, $K_{MG^+}^{CD}$, k_w and k_{CD} values were obtained as $(5.57 \pm 0.30) \times 10^3 \text{ mol}^{-1} \text{ dm}^3$, $(5.52 \pm 0.25) \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ and $(1.44 \pm 0.025) \times 10^{-2} \text{ s}^{-1}$ respectively. The obtained value of k_w $\{(5.52 \pm 0.25) \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}\}$ from the fitting corresponds to the rate constant obtained from our work in pure water ($5.50 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$). The other values of $K_{MG^+}^{CD}$ and k_{CD} are consistency with literature values from similar system.¹²

3. 2. Effect of Hexadecyltrimethylammonium Bromide (CTAB) on the Hydrolysis of Malachite Green

Figure 2 shows a plot of k_{obs} versus [CTAB]. The concentration of CTAB ranges from pre- to the post-micellar regions. The profile is structured. At low [CTAB], there is little or no change in the observed rate constant (k_{obs}) up to $0.0006 \text{ mol dm}^{-3}$ which is an indication of weak pre-micellar activity. This behaviour is similar to that observed in CV/CTACl system¹². The k_{obs} – [CTAB] is followed by a rapid increase in k_{obs} which latter shows saturation at [CTAB] greater than $0.0026 \text{ mol dm}^{-3}$. The concentration of malachite green was kept constant at $5.77 \times 10^{-5} \text{ mol dm}^{-3}$ as in previous work on β – CD to avoid complication that may arise from the dependence of the hydrolysis on concentration of MG^+ .

The effect of micellar systems on chemical reactions is usually analyzed in terms of the micellar pseudophase model which assumes that the reactants are partitioned between the aqueous and micellar pseudophases. The variation of the rate constant with surfactant concentration is treated as shown in scheme 2:



The substrate MG^+ is assumed to bind with the surfactant D_n with a binding constant $K_{MG^+}^m$. k_w and k_m are the first-order rate constants for the reaction in aqueous and micellar pseudophases respectively.

This model leads to the following relationship for micelle-catalyzed reaction;

$$k_{obs} = \frac{k_w [D]^n + k_m K_{MG^+}^m}{K_{MG^+}^m + [D]^n} \quad (4)$$

The experimental results were fitted by means of a non-linear regression analysis using MicroMath Scientist for windows software (figure 2). The value of k_w was kept constant and was equal to the value previously obtained in pure water. The values of $K_{MG^+}^m$ and k_m were $(1.069 \pm$

$0.020) \times 10^{-10} \text{ mol}^{-1} \text{ dm}^3$ and $(0.036 \pm 0.020) \text{ s}^{-1}$ respectively and are summarized in Table 1.

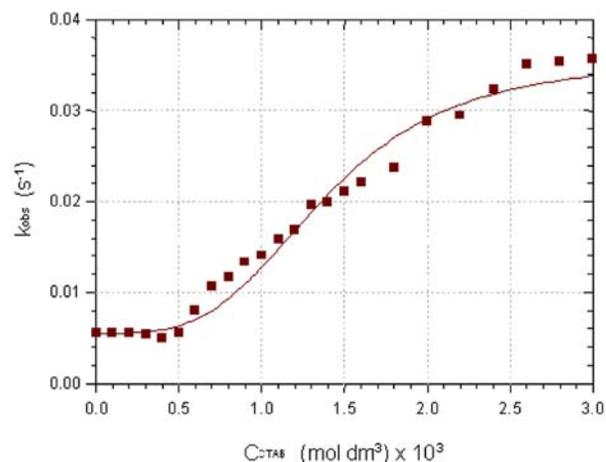


Figure 2: The effect of CTAB on the observed rate constant (k_{obs}) of the base hydrolysis of malachite green at 25 °C. $[OH^-] = 0.001 \text{ mol dm}^{-3}$. Unbroken line is theoretical value from the model.

3. 3. Effect of CTAB/ β -CD Mixed Systems on the Hydrolysis of Malachite Green

The effect of concentration of CTAB on the observed rate constant k_{obs} in the presence of β -CD was determined by varying [CTAB] in pre-micellar and post-micellar regions. The experiments were determined at fixed β -CD concentrations of 0.0003, 0.001 and 0.002 mol dm^{-3} . In each of the fixed β -CD concentration the observed rate constant show the same kind of [CTAB] dependence as observed in the absence of CD (Figure 2). On comparing the profiles at different [CD], it was observed that at [CTAB] less than $0.001 \text{ mol dm}^{-3}$, the increase in [CD] catalysed the reaction while the reverse was the case at [CTAB] greater than $0.002 \text{ mol dm}^{-3}$ (Figure 3). The presence of CD increases the apparent cmc of the CTAB as can be seen in Figure 3.

Table 1: Kinetic parameters for the basic hydrolysis of MG^+ in CTAB/CD mixed systems

[CD] (mol dm^{-3})	$K_{MG^+}^m$ ($\text{mol}^{-1} \text{ dm}^3$)	k_m (s^{-1}) (± 0.020)	n (± 0.3)
0.0000	$(1.069 \pm 0.020) \times 10^{-10}$	0.0365	3.5
0.0003	$(1.216 \pm 0.018) \times 10^{-11}$	0.0442	4.1
0.0010	$(1.431 \pm 0.020) \times 10^{-11}$	0.0457	5.5
0.0020	$(2.093 \pm 0.020) \times 10^{-25}$	0.0468	10.2

Applying the model in equation 3.4 to the data in CTAB/CD mixed system by the same curve fitting procedure, the values of $K_{MG^+}^m$ and k_m were obtained and summarized in table 1. The value of k_m increases slightly as the [CD] increases. This is an indication that most of the reac-

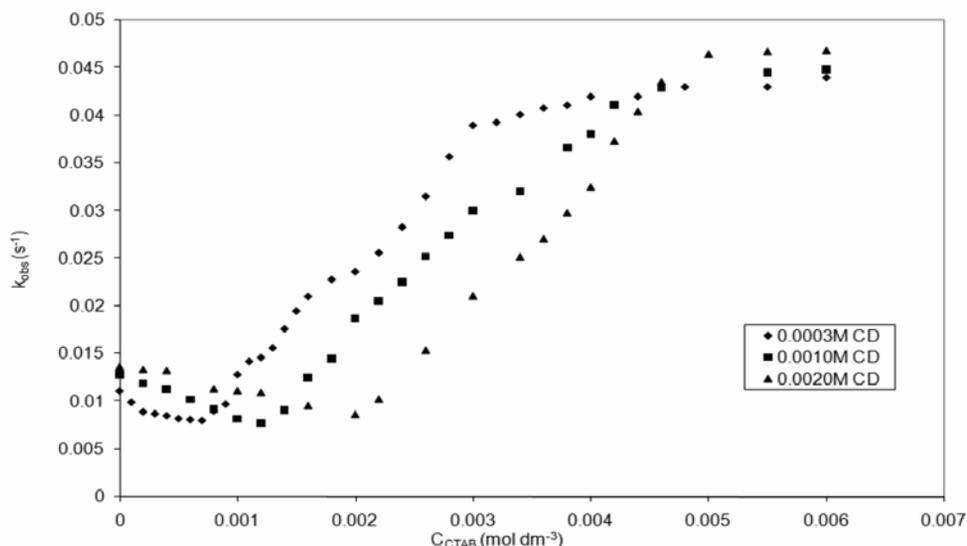


Figure 3: Effect of observed rate constant (k_{obs}) on concentration of CTAB at constant CD concentration of 0.0003, 0.0010 and 0.0020 mol dm⁻³.

tion takes place in the bulk water region. The values of the binding constants $K_{MG^+}^m$ are very small indicating that the dissociation of the bounded substrate and surfactant to its free component is negligible. As the [CD] increases the value of binding constant ($K_{MG^+}^m$) decreases rapidly because the CD inclusions of CTAB monomer compete with the micellization of the CTAB thereby delaying the formation of micellar system. The fact that n , increases with [CD] implies that the number of surfactant monomers required for aggregate formation increases with [CD] as shown in Table 1. This is consistent with increase in critical micelle concentration (c.m.c) of surfactant in the presence of CD.

4. Conclusion

The observed rate constants in the presence and the absence of CD are an indication that interaction between the micellar system and cyclodextrin does not take place. The major effect of CD on the reaction is the competition between the surfactant monomers binding to the cyclodextrin and their self association. The presence of CD enhances micellization by lowering the cmc. The pseudophase model applied to the data satisfied the CD-catalyzed reaction as well as the CTAB catalyzed reaction.

Povzetek

Raziskovali smo kinetiko hidrolize barvila malahit zeleno v mešanici β -ciklodekstrina (β -CD) in cetiltrimetilamonijeva bromida (CTAB) pri 25 °C. Ugotovili smo, da konstanta hitrosti reakcije (k_{obs}) narašča z rastočo koncentracijo β -CD vse do nasičenja, medtem ko je pri konstantni koncentraciji β -CD odvisna od koncentracije CTAB. Kinetična analiza kaže, da je odločilna kompleksacija β -CD z monomerami surfaktanta, ki zavira tvorbo micel. Dobljeni rezultati kažejo, da proces micelizacije lahko opišemo s na pseudofaznim modelom micelizacije.

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