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Article

# Alkaline Fading of Malachite Green in $\beta$ -Cyclodextrins

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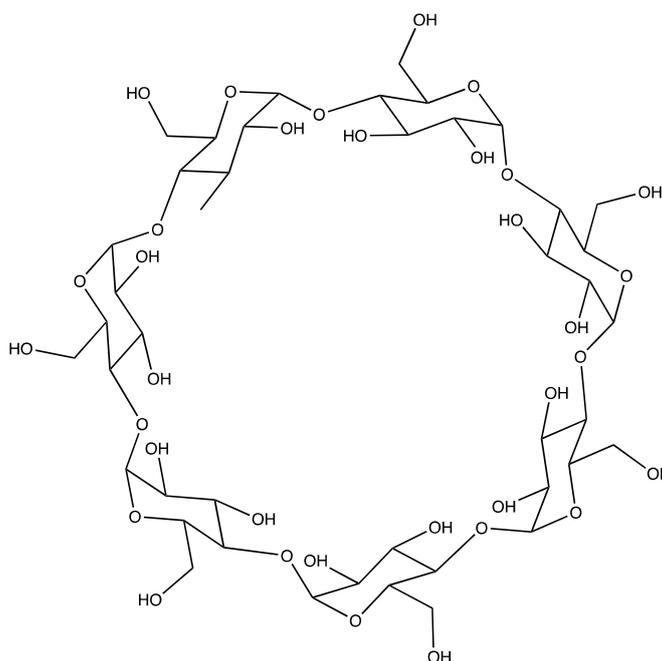
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**Abstract:** The basic hydrolysis of Malachite Green (MG) in the presence of  $\beta$ -Cyclodextrin has been studied and a catalytic effect has been found. Indeed, this basic hydrolysis is catalyzed by the interaction of deprotonated cyclodextrin hydroxyl group with the carbocation in the host-guest complex. This behavior is like the hydrolysis of Cristal Violet (CV) in the same reaction media.

**Keywords:** basic hydrolysis; alkaline fading; cyclodextrin; host-guest complex; catalysis

## 1. Introduction

Cyclic oligosaccharides made up of several glucose units linked together by  $\alpha$ -1,4 glycosidic bonds are known as cyclodextrins (CDs) [1–3]. Normally this family of compounds is formed by structures of between six and eight glucopyranosides ( $\alpha$ -Cd,  $\beta$ -CD,  $\gamma$ -CD, and  $\delta$ -CD respectively)[4], see Scheme 1.

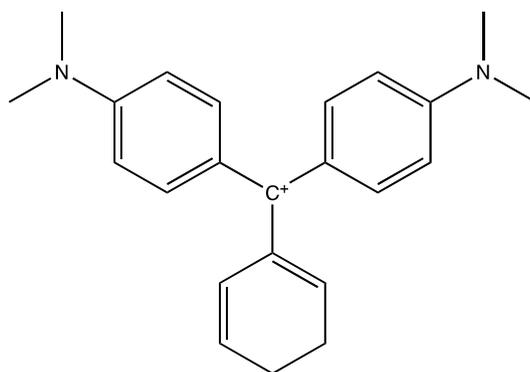


**Scheme 1.** Chemical structure of  $\beta$ -cyclodextrins.

Topologically, these compounds have a toroidal shape whose openings are exposed to the primary and secondary hydroxyl groups of the glucopyranose [5]. Due to this peculiar structure, the interior cavity of the cone has a lower hydrophilic character as compared to its exterior, which is hydrophilic in nature, with which it is capable of harboring hydrophobic molecules inside, giving rise to inclusion complexes (the host-guest system) through non-covalent interactions when the size, shape and polarity of these molecules is adequate [5,6]. The stabilization of the guest molecule is

given by different factors being Van der Waals and hydrophobic forces or H-bonds, among others [7]. In any case, the study of these inclusion complexes is a key part of what is known as supramolecular chemistry [8,9]. Another interesting aspect of CDs is they can modulate the reactivity related with their capacity to form guest host complexes with small and medium sized molecules [10]. According to Iglesias and Fernández (1998) [10], these changes in reactivity are the result of host-host interactions and vary significantly depending on the nature of the reagents and the reaction. In this way we can observe both increases and decreases in the reaction speed, with which in some cases CD have been used as stabilizers and in others as potential phase transfer catalysts. In addition, in some cases CDs can participate directly in the chemical reaction [10].

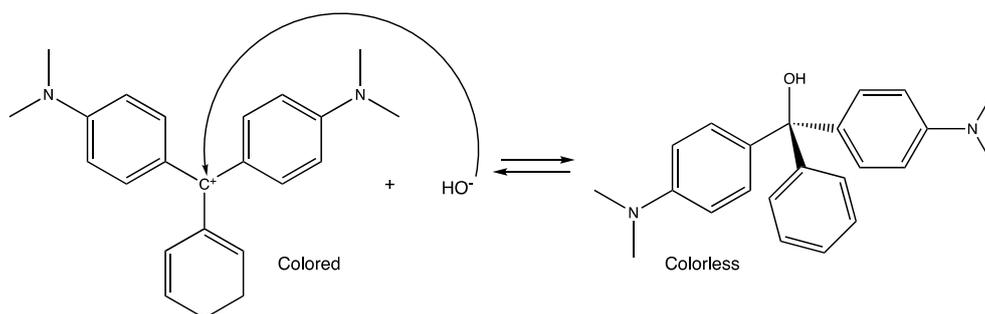
Malachite green (MG) is a triphenylmethane cationic dye—Scheme 2—which is used in the pigment industry [11] to color silk, wool and leather [12]. This compound is also used as a therapeutic agent for fish, since this compound present antifungal activity [13]. The common name of this compound is associated with its intense green color [14], presenting a strong absorption band in the VIS region at  $\lambda=621\text{nm}$ , with an extinction coefficient of  $\epsilon=10^5\text{M}^{-1}\text{cm}^{-1}$  ( $\log \epsilon$  [15]. This band disappears during the hydrolysis process, changing from a colored compound to a colorless compound, which facilitates its spectrophotometric monitoring and is the reason why it is a very popular reaction in chemical kinetics labs in undergraduate studies, as occurs with his analogous compound Crystal violet (CV) [11].



**Scheme 2.** Malachite Green (MG), 4-[[4-(Dimethylamino) phenyl] (phenyl)methylidene]-*N,N*-dimethylcyclohexa-2,5-dien-1-iminium.

In relation to the uses of MG in commercial aquaculture and ornamental aquariums, a controversial application is its use as an antimicrobial agent for the treatment of the oomycete fungi on fish and fish eggs because its adverse effects on human immune and reproductive systems [16]. Different studies concluded the important fungal effect against oomycete fungus such as *Saprolegnia* [17], *Haliphthoros* [18] or *Aphanomyces invades* [19]. Due to its effects on health, numerous studies in the literature analyze the physical-chemical properties of this compound [14,20–22].

According to Leis et al. (1993) the MG alkaline fading is a reaction with a long chemical tradition [23]. It takes place through a nucleophilic attack of the  $\text{OH}^-$  on the carbocation [24] -Scheme 3-. This hydrolysis, together with that of other analogs (such as crystal violet -CV-) was used for the construction of the Ritchie  $\text{N}^+$  nucleophilicity scale [25].



**Scheme 3.** Malachite Green basic hydrolysis reaction mechanism.

Our aim is to evaluate the effect exerted by the presence of  $\beta$ -Cyclodextrin on the basic hydrolysis of malachite green.

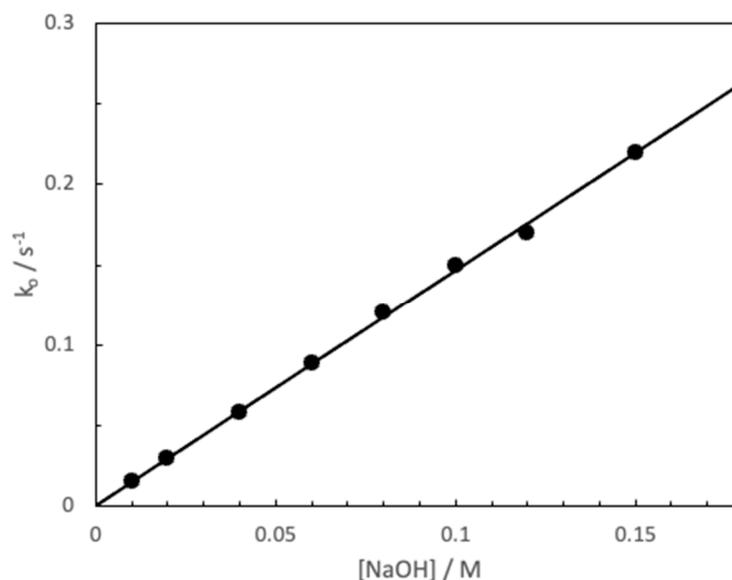
## 2. Materials and Methods

Sigma supplied  $\beta$ -CD in the highest purity available and it was used as received, keeping in mind that commercial  $\beta$ -CD has an H<sub>2</sub>O content of 8 mol/mol. It was deprotonated under the alkaline conditions used ( $[\text{NaOH}] > 0.1 \text{ M}$ ) ( $\text{pK}_a \text{ CD} = 12.2$ ) [26]. Due to the deprotonation of  $\beta$ -CD,  $[\text{OH}^-]$  was obtained by subtracting the concentration of CD from that of NaOH. NaOH and MG were supplied by Aldrich. NaOH solutions were titrated with potassium hydrogen phthalate.

The reaction was followed by UV-Vis spectroscopy, monitoring the disappearance of the MG in the band of  $\lambda = 621 \text{ nm}$  using a Variant Cari 60 spectrophotometer. All the experiments were carried out at  $25.0 \pm 0.1^\circ\text{C}$  using a thermostat-cryostat supplied by Poly-Science. The kinetic experiments were carried out under pseudo-first order conditions, keeping the concentration of MG (approx.  $10^{-5} \text{ M}$ ) always much lower than that of NaOH. The obtained absorbance/time data were fitted by first order integrated equations, and the values of the pseudo first order rate constants ( $k_o$ ) were reproducible to within 3%.

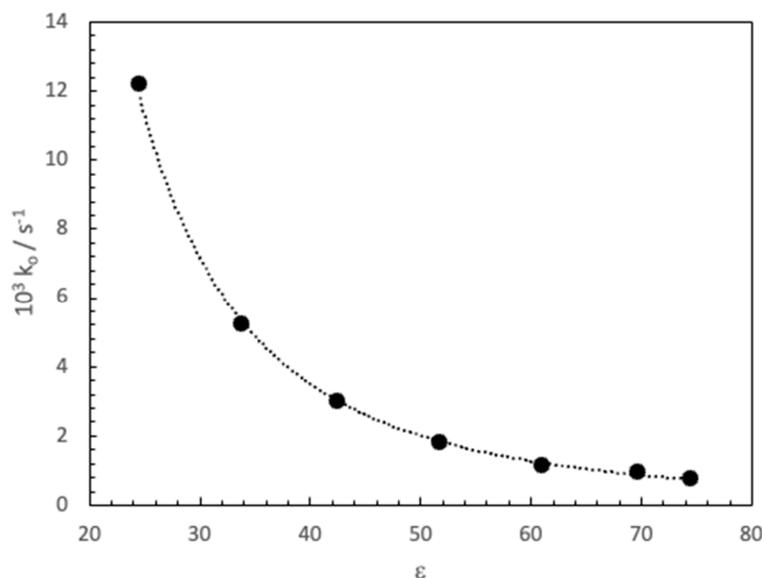
## 3. Results and Discussion

The rate constant of the basic hydrolysis of MG in water was determined to maintain consistency with the results obtained throughout this work. The constant was determined by varying the  $[\text{NaOH}]$  (0.01 M-0.15 M) keeping the  $[\text{MG}]$  constant ( $10^{-5} \text{ M}$ ). Figure 1 shows the dependence of the observed rate constant of pseudo first order ( $k_o$ ) and  $[\text{NaOH}]$ , from which a value for  $k_w = 1.46 \pm 0.03 \text{ M}^{-1}\text{s}^{-1}$  has been obtained ( $R^2 = 0.9986$ ). This value is compatible with previous one in the literature [23,27].



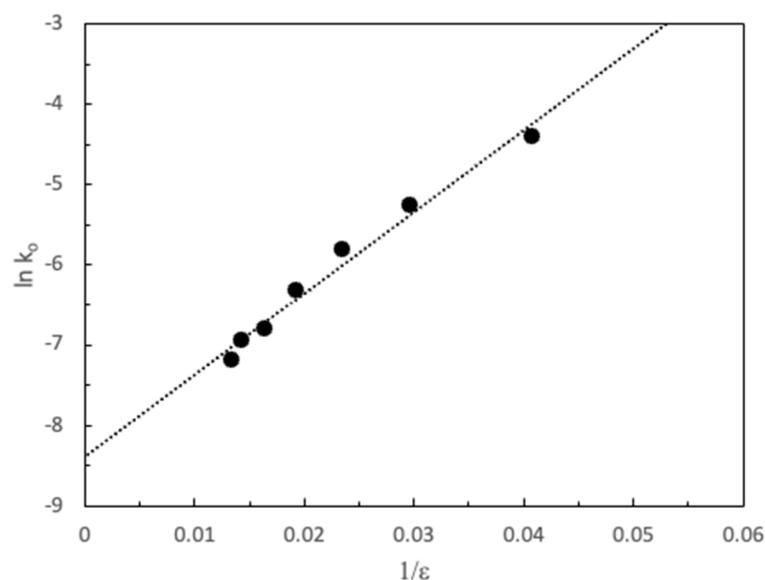
**Figure 1.** Influence of  $[\text{NaOH}]$  upon the pseudo first order rate constant,  $k_o$ , of alkaline fading of MG.  $[\text{MG}] = 10^{-5} \text{ M}$ ,  $T = 25^\circ\text{C}$ .

Since the cyclodextrin cavity has a lower polarity than that of bulk water, the influence of the dielectric constant ( $\epsilon$ ) on the MG basic hydrolysis reaction has also been analyzed using dioxane-water mixtures. For this,  $\epsilon$  value was varied between 24.54 and 74.43, maintaining a constant MG and NaOH concentrations ( $[\text{MG}] = 1.46 \times 10^{-5} \text{ M}$  and  $[\text{NaOH}] = 9.98 \times 10^{-4} \text{ M}$ ). A significant decrease in the rate constant was observed as the dielectric constant increased (Figure 2).



**Figure 2.** Variation of the pseudo-first order rate constant,  $k_0$ , with the dielectric constant (dioxane-water mixtures) for the basic hydrolysis of MG. ( $[MG]=1.46 \times 10^{-5} M$  and  $[NaOH]=9.98 \times 10^{-4} M$ ,  $T=25^\circ C$ ).

An interesting piece of information would be the evaluation of the radius of the activated complex for the reaction using the double sphere model [28]. From the fits of the experimental data to equation (1) -where  $z_A$  and  $z_B$  are the ions charge,  $e$  is the electron charge, the dielectric constant,  $\sigma^\ddagger$  is the active complex radius and  $k^0$  is the rate constant in a high dielectric constant medium ( $\epsilon=\infty$ ) - (Figure 3) we obtain a value for the radius of the complex  $\sigma^\ddagger$  5.1 Å ( $R^2=0.9803$ ).

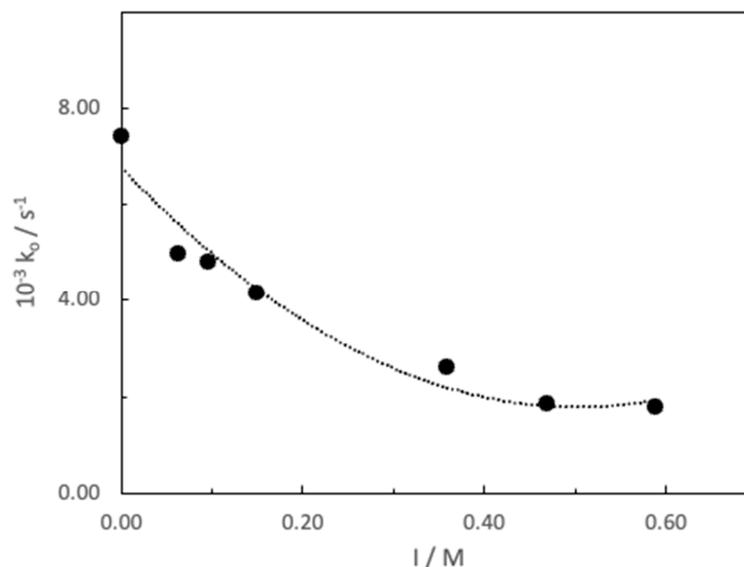


**Figure 3.** Double sphere model applied to the influence of the dielectric constant on the pseudo-first order rate constant,  $k_0$ , for the basic hydrolysis of MG. ( $[MG]=1.46 \times 10^{-5} M$  and  $[NaOH]=9.98 \times 10^{-4} M$ ,  $T=25^\circ C$ ).

$$\ln k = \ln k^0 - \frac{z_A z_B e^2}{\epsilon \sigma^\ddagger k_B T} \quad (1)$$

After determining the influence of the dielectric constant on the alkaline fading of MG, a study of the ionic strength on the rate constant of the hydrolysis process has been carried out.  $NaClO_4$  was used as electrolyte to set the ionic strength, which varied between  $4.99 \times 10^{-4}$  and 0.59M. As would be

expected, a decrease in the rate constant is observed as the ionic strength of the medium increases (Figure 4).



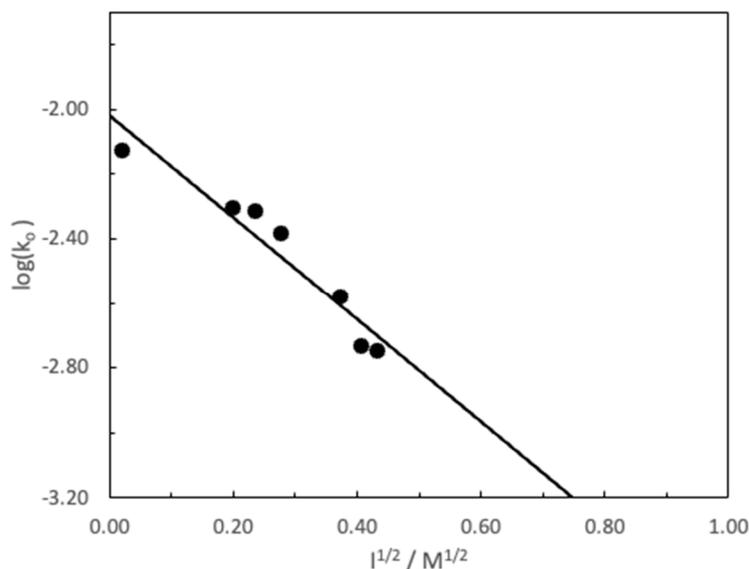
**Figure 4.** Influence of ionic strength on the pseudo-first-order constant,  $k_0$ , for the basic hydrolysis of MG -ionic strength fixed with  $\text{NaClO}_4^-$  ( $[\text{MG}]=7.33 \times 10^{-6} \text{M}$  and  $[\text{NaOH}]=4.99 \times 10^{-3} \text{M}$ ,  $T=25^\circ\text{C}$ ).

The values obtained fit the Brönsted-Bjerrum equation - Equation (2) - based on a simple Debye model [29].

$$\ln k = \ln k^0 + 1.02 z_A z_B \frac{\sqrt{I}}{1 + \sqrt{I}} \quad (2)$$

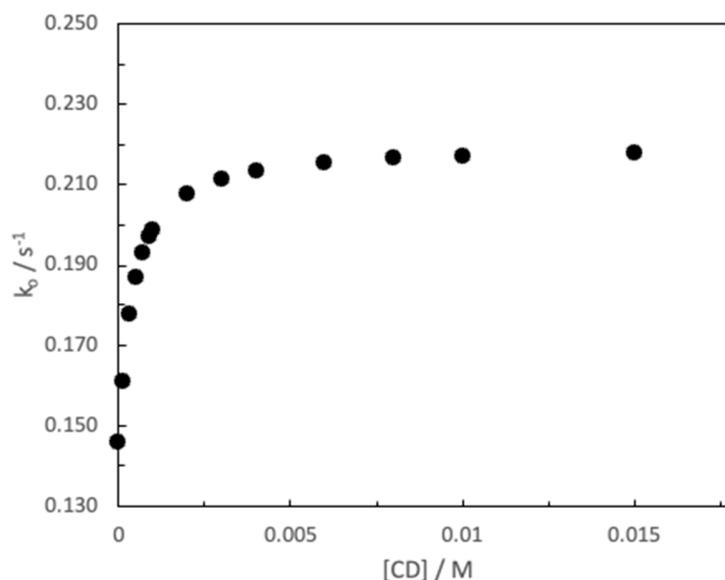
where  $z_A$  and  $z_B$  are the ions charge,  $I$  is the ionic strength and  $k^0$  is the rate constant at  $I=0$ .

Figure 5 shows the fit of experimental data to Equation (2) ( $R^2=0.9203$ ). Obviously, the fulfillment of this equation is fortuitous, because the Debye model is only valid for very low ionic strengths. However, it is relatively common that the data on the variation of the reaction rate with the ionic strength between ionic species (in our case  $\text{MG}^+$  and  $\text{HO}^-$ ) fit in a "formal" way to the Debye model, however, it is not possible to rigorously identify the parameters in contracts with which the Debye model assigns. In any case, the inhibition of the reaction by increasing the salinity of the medium is in accordance with all the predictions from simple electrostatic theories [29]. It should be noted that unlike happened with CV, no anomalous behavior is observed between the carbocation and  $\text{ClO}_4^-$ . This would indicate that in the case of MG, unlike what occurs with CV, ion pairs are not formed between these two species [30].



**Figure 5.** Influence of ionic strength on the pseudo-first-order constant,  $k_o$ , for the basic hydrolysis of MG ( $[MG]=7.33 \times 10^{-6} M$  and  $[NaOH]=4.99 \times 10^{-3} M$ ,  $T=25^\circ C$ ) -ionic strength fixed with  $NaClO_4$ .

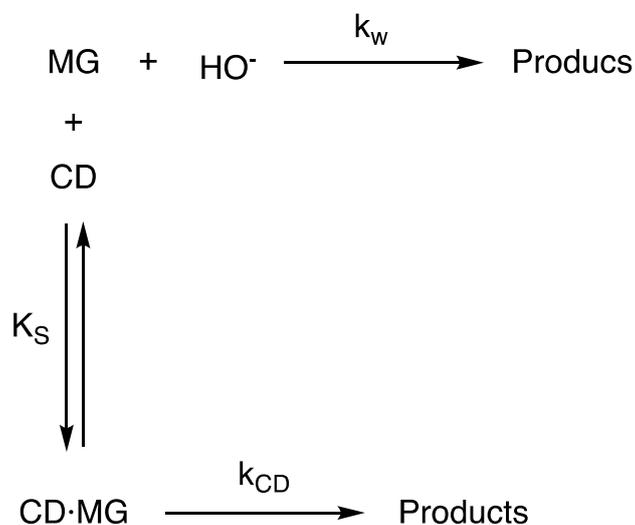
Once the basic hydrolysis reaction of MG in an aqueous media has been characterized, the alkaline hydrolysis of MG in the presence of  $\beta$ -CD has been analyzed, the alkaline hydrolysis of MG in the presence of  $\beta$ -CD has been analyzed. The hydrolysis reaction is assessed by varying  $[CD]$  between 0 and 0.015 M. As can be seen in Figure 6, a catalytic effect of  $\beta$ -CD is observed in this reaction.



**Figure 6.** Influence of  $\beta$ -CD concentration on the pseudo-first-order constant,  $k_o$ , for the basic hydrolysis of MG. ( $[MG]=1.46 \times 10^{-5} M$  and  $[NaOH]=0.1 M$ ,  $T=25^\circ C$ ).

This observed catalysis is consistent with the possibility of a nucleophilic attack by an ionized CD hydroxyl group on the  $MG^+$  associated with the CD [24]. This behavior is like that reported in the literature (i.e., cleavage of aryl esters in the presence of CD [31,32] or that observed for CV hydrolysis [33,34]). A direct attack of  $OH^-$  on the MG that is associated with the MG-CD complex should be ruled out, since given the important effect of the dielectric constant on the reaction rate (*vide supra*), it would imply a greater catalytic effect of the presence of cyclodextrins in the medium.

Applying the model presented in Scheme 4, assuming a substrate that undergoes an uncatalyzed reaction in each medium and a catalyzed reaction through a 1:1 substrate/CD complex. In the scheme,  $k_w$  corresponds with the rate constant in the bulk water,  $k_{CD}$  is the catalytic rate constant in the presence of CD and  $K_s$  is the binding constant of MG to the CD cavity.

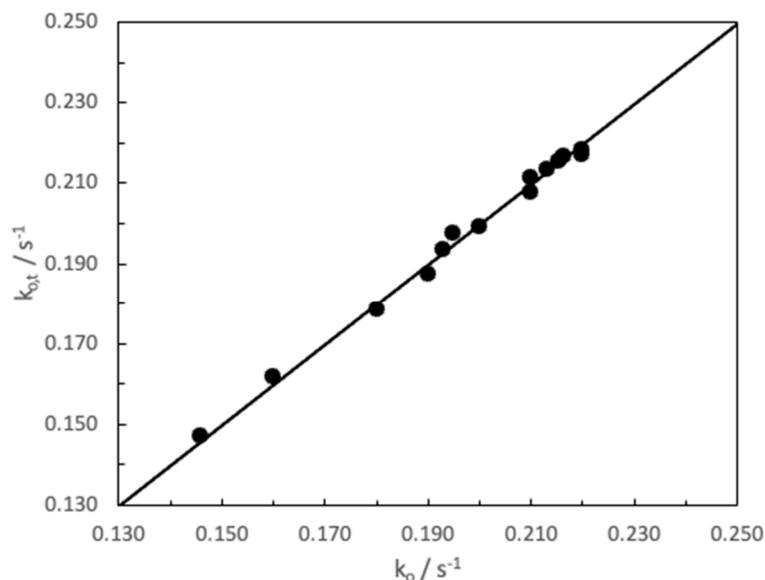


**Scheme 4.** Mechanism of basic hydrolysis of MG in the presence of CD.

From this mechanism using the rate equations and the formation equilibrium of the inclusion complex, Equation (3) can be easily obtained [34].

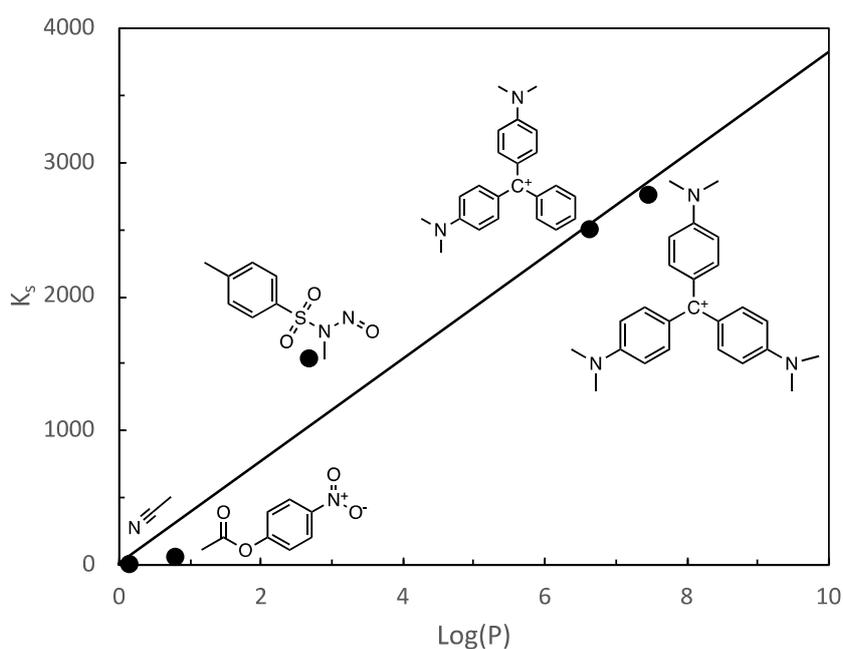
$$k_o = \frac{k_w[\text{HO}^-] + k_{CD}K_s[\text{CD}]}{1 + K_s[\text{CD}]} \quad (3)$$

The fit of equation (2) to the experiment results yields a value of  $k_w = 1.47 \pm 0.01 \text{ mol}^{-1} \cdot \text{s}^{-1}$ , which is compatible with the value obtained in water  $k_w = 1.46 \pm 0.03 \text{ M}^{-1}\text{s}^{-1}$  (vide supra) [23]. The value of catalytic constant in the presence of CD was estimated as  $k_{CD} = 0.25 \pm 0.03 \text{ s}^{-1}$ . In this sense the ratio  $k_{CD}/k_w$  was 0.17, which is so close to the equivalent ratio for basic hydrolysis of CV ( $k_{CD}/k_w = 0.15$ ) obtained in previous experiments [30]. The binding constant of MG to CD was evaluated in  $K_s = 2500 \pm 50$ . Figure 7 shows the experimental results compared to those obtained from adjusting them to equation (1). As can be, this was satisfactory. Indeed, the solid line represents the adjustment of  $k_o$  and  $k_{o,t}$  values to the slope 1 line, for which a value of  $R^2 = 0.9989$  has been obtained. This  $R^2$  value demonstrates the good fit of the theoretical model to the experimental data.



**Figure 7.** Experimental results ( $k_o$ ) vs. theoretical results ( $k_{o,t}$ ) predicted by eq. 3 obtained from scheme 4 ( $[MG]=1.46 \times 10^{-5} M$  and  $[NaOH]=0.1 M$ ,  $T=25^\circ C$ ).

Another aspect to underline, which confirms the validity of the model, is the value obtained for the MG binding constant to cyclodextrin cavity. As quote above, a value of  $K_s=2500$  has been obtained, which is like the CV value obtained in the literature ( $K_s=2750$ ) [24]. The ratio between MG and CV binding constant is 0.91 which is too close to the  $\log(P)$  ratio between MG and CV equal to 0.89,  $\log(P)_{MG} = 6.65$  and  $\log(P)_{CV} = 7.48$ . In fact, if we compare the values of the association constants of different substrates taken from the literature, an acceptable correlation can be observed between the values of the formation constants of the host-guest complexes and the  $\log(P)$  values of the substrates [31,32,34]. This linear relationship is shown in Figure 8 ( $R^2=0.9514$ ). This correlation found between the formation constant of the host-guest complex and the substrates would demonstrate that the main driving force of the formation of said complexes is associated with their hydrophobicity [35].



**Figure 8.** Relationship between the host-guest complexes formation constant and the log (P) values of substrates.

#### 4. Conclusions

A comparison of the rate constants observed in the presence and absence of CD reveals that a catalysis of the hydrolysis process associated with the reaction between the MG and the deprotonated cyclodextrin occurs, with no evidence being observed that an attack by HO<sup>-</sup> on the MG-CD inclusion complex. The proposed model has been successfully applied to a reaction catalyzed by CD. The model considers two simultaneous pathways in the aqueous medium involving free hydroxyl ions and the substrate-CD complex, respectively. The values obtained for both the kinetic constants and the equilibrium constant are in line with values of similar substances in the literature.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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