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Influence of β-Cyclodextrins upon the Degradation of Carbofuran Derivatives under Alkaline Conditions

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Abstract

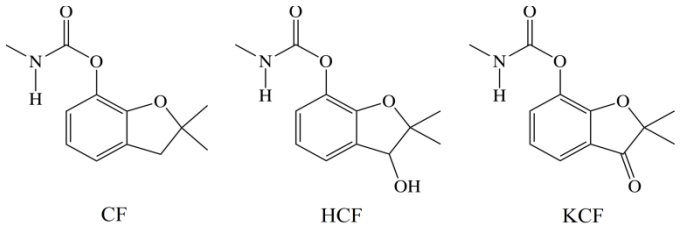
The influence of β-cyclodextrins (β-CDs) on the stability carbufuran-derivatives (3-keto-carbofuran –KCF- and 2-hydroxy carbufuran –HCF-) in basic media has been analysed. An inhibition in the basic hydrolysis has been observed. The observed rate constant decreases because of the formation of an unreactive host-guest complex between carbofuran and derivatives and the CDs. The CDs protect the carbamates increasing their half-life time in the presence of basic conditions.

Keywords

carbofuran, 3-keto-carbofuran, 3-hydroxy-carbofuran, β-cyclodextrin, inclusion complex, host–guest, degradation.

Introduction

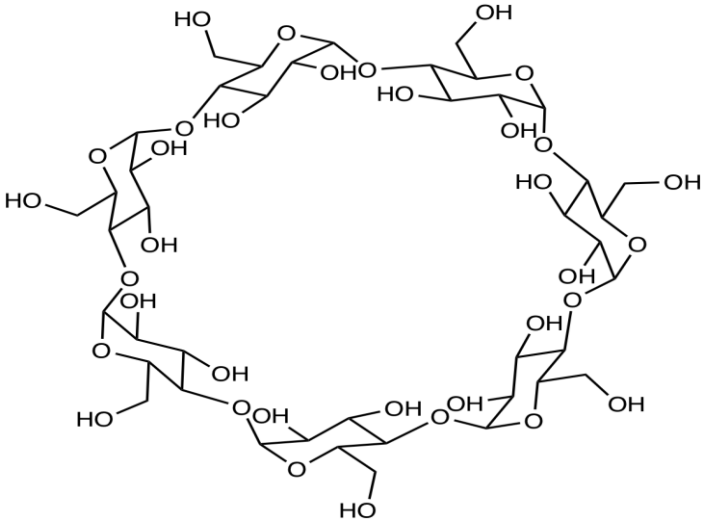
Nowadays, the application of numerous pesticides has become inevitable to protect plantations from diseases and pests. Carbofuran (CF), 3-hydroxy-carbofuran (HCF) and 3-keto-carbofuran (KCF) –see scheme 1- are three of the most toxic carbamate pesticides used to control insects in many crops as potatoes, corn, citric, soybeans or turf grass [1]. They are systemic and contact insecticides and nematicides that act as cholinesterase inhibitors [2]. Further, pesticide pollution has added plenty of compounds to the environment as pollutants increasing concern among the public [3]. In soils, these carbamates are moderately persistent with a half-life ranging from 30 and 120 days depending on environmental conditions [4-9]. On the other hand, hydrolysis processes are one of the main pathways for the degradation of many xenobiotics in the environment [4-6,10-11]. Finally, CF, HCK and KCF are relatively soluble in water, as compared with other xenobiotics, and highly mobile in soils [12].



Scheme 1: Molecules of Carbofuran (CF), 3-hydroxy-carbofuran (HCF) and 3-keto-carbofuran

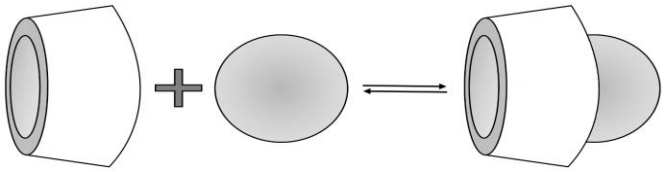
The fact is that many pesticides can form inclusion with CD –see scheme 2 and 3-, often resulting in improvements in the properties of the complexed substances. Sometimes in a combination of pesticide-CD take place, when the [CD] increases, the inclusion complex precipitated out of solution and reduces the mobility of the pesticide.

Also, in other cases, the observed behaviour is the opposite, CDs may form CD-pesticide inclusion complexes where it is more soluble than the free solute in a polar solvent. For this reason, CDs were successfully used to extract numerous commonly used pesticides from contaminated soil via cyclodextrin complexation [13-16]. In fact, that is a more environmentally friendly method compared to surfactants and organic solvents. CDs might become a great alternative as agents for improve remediation of contaminated soil and groundwater [17-22]. The must be kept in mind that the cost of cyclodextrins is declining it would be interesting to use in the pesticide solutions formulations to improve their biological activity [23].



Scheme 2: β-Cyclodextrin

In previous papers, our research group analyse the influence of α-CD, β-CD and γ-CD upon the basic hydrolysis of carbofuran [24]. In this study, we were interested in compare whether β–CDs can change the stability of three carbamates (carbofuran and two carbofuran-derivatives) in basic media.



Scheme 3: Cyclodextrin host-guest complex formation.

Materals and Methods

β-CD, 3-hydroxy-2,3-dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate and 3-keto-2,3- dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate, better known as 3-hydroxy-carbofuran and 3-keto-carbofuran respectively, were supplied by Sigma-Aldrich (Germany) and sodium hydroxide and acetonitrile were supplied by Panreac (Spain) [24]. Water was double-distilled and degasified to prepare by weight all the aqueous solutions, beside this, all reagents used in the present research were of the maximum commercial purity and were used without further purification [24]. Experimental data of carbofuran was taken from the literature [24].

The kinetic tests were conducted under pseudo first-order conditions ([PESTICIDE] << [OH^-]). Reactions were monitored through the first-order basic hydrolysis of carbofuran-derivatives using a Varian Cary 50 Bio spectrophotometer with an observation cell thermostated at 25.0 ± 0.1 °C using a Polyscience thermostat-cryostat temperature controller. When it was necessary, a rapid mixing stopped-flow unit supplied by Applied Photophysics, thermostated at 25.0 ± 0.1 °C (with a Polyscience thermostat-cryostat) was used. Detailed experimental procedure has been described elsewhere [24].

Nonlinear regressions were carried out in a commercial software (pro Fit 6.2) supplied by QuantumSoft (Switzerland).

Results

To guarantee that the presence of β-CDs would not the reaction product, a reaction spectra were carried out between 200 and 800 nm, and due to that β-CDs absorb in the UV-vis region, the spectrum of β-CDs in absence of reaction was used as blank. In each instance, it was observed that the final spectrum coincided with the spectrum obtained in pure water (data not shown).

The influence of β-CDs upon the basic hydrolysis of carbofuran-derivatives has been analysed in the present manuscript. Pseudo-first order conditions were kept in all the experiments. Carbofuran-derivatives concentration was kept in all of experiments and equal to 8.33×10^{-5} M. This concentration was chosen to optimize the change in absorbance with time during the kinetic process. Sodium hydroxide concentrations were chosen to obtain a suitable half-life time to monitor the reaction. Finally, β-CDs concentration was varied between 0 and 0.017 M.

The disappearance of the absorbance at its maximum wavelength, (λ= 290 nm and λ= 280 nm KCF and HCF respectively) was used to follow spectropho to metrically the reaction advance. Rate equation is the following:

$$-\frac{d[\text{products}]}{dt} = k_w[3\text{HCF}_t][\text{OH}_t^-] = k_{obs}[3\text{HCF}_t] = k_{obs}([3\text{HCF}_0] - [3\text{HCF}_t]) \quad (1)$$

$$-\frac{d[\text{products}]}{dt} = k_w[3\text{KCF}_t][\text{OH}_t^-] = k_{obs}[3\text{KCF}_t] = k_{obs}([3\text{KCF}_0] - [3\text{KCF}_t]) \quad (2)$$

where [3HCF] and [3KCF] are the carbofuran-derivative concentrations: 3-hydroxy-carbofuran (equation 1) and 3-keto-carbofuran (equation 2). k_w and k_{obs} are the bimolecular rate and the pseudo-first rate constants for the hydrolysis reaction. These equations can be integrated, and expressing the concentration of carbofuran-derivatives in terms of absorbance, yields:

$$A_t = A_0 \exp(-k_{obs}\, t) + A_\infty\, (1 - \exp(-k_{obs}\, t)) \quad (3)$$

Figures 1-2 shows the influence of [OH^-] on k_{obs} in pure water and in β-CDs, respectively. As can be observed a linear dependence between the pseudo-first order rate constant and [OH^-] was obtained for each substrate.

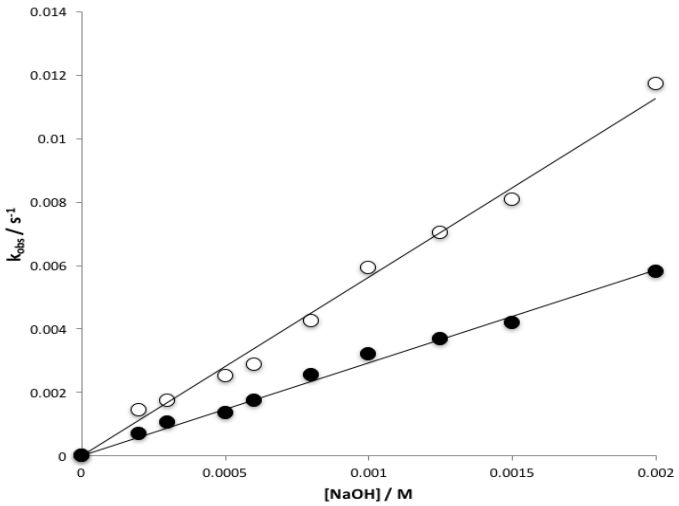


Figure 1: Influence of [NaOH] upon the basic hydrolysis of HCF, (○) in water (T=25ºC, [HCF]=8.33×10^{-5}M) and (●) in presence of β-CD. (T=25ºC, [HCF]=8.33×10^{-5}M, [β-CD]=6.67×10^{-3}M). Solid lines represent the fit of the experimental data to a line $k_{obs}=k_2$[NaOH]. R values are (○) R=0.9961 and (●) R=0.9964.

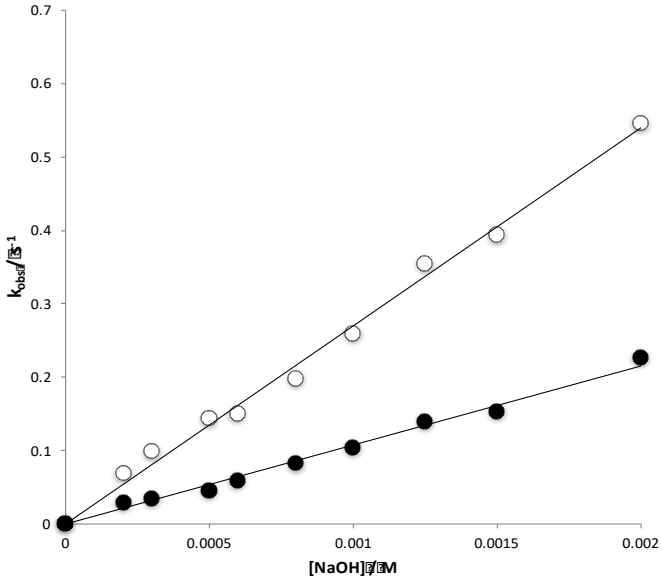


Figure 2: Influence of [NaOH] upon the basic hydrolysis of KCF, (○) in water (T=25ºC, [KCF]=8.33×10^{-5}M) and (●) in presence of β-CD. (T=25ºC, [KCF]=8.33×10^{-5}M, [β-CD]=6.67×10^{-3}M). Solid lines represent the fit of the experimental data to a line $k_{obs}=k_2$[NaOH]. R values are (○) R=0.9968 and (●) R=0.9953

A large inhibition has been observed for the basic hydrolysis (Figures 3-4). Hence, 3-hydroxy-carbofuran presents a 3.3 times-fold inhibition and 3-keto-carbofuran yields 3.8 times-fold inhibition. This result is consistent with the corresponding one observed for hydrolysis of carbofuran (4.5 times-fold) [24]. This inhibition probes host-guest complex formation between both carbamates and □-CD.

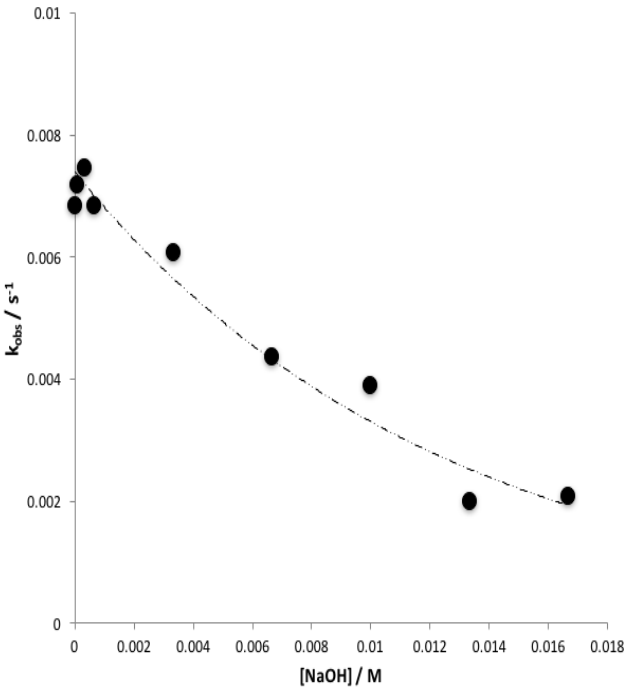


Figure 3: Influence of [β-CD] upon the basic hydrolysis of HCF (T=25ºC, [HCF]=8.33×10^{-5}M, [NaOH]= 1.00×10^{-3}M).

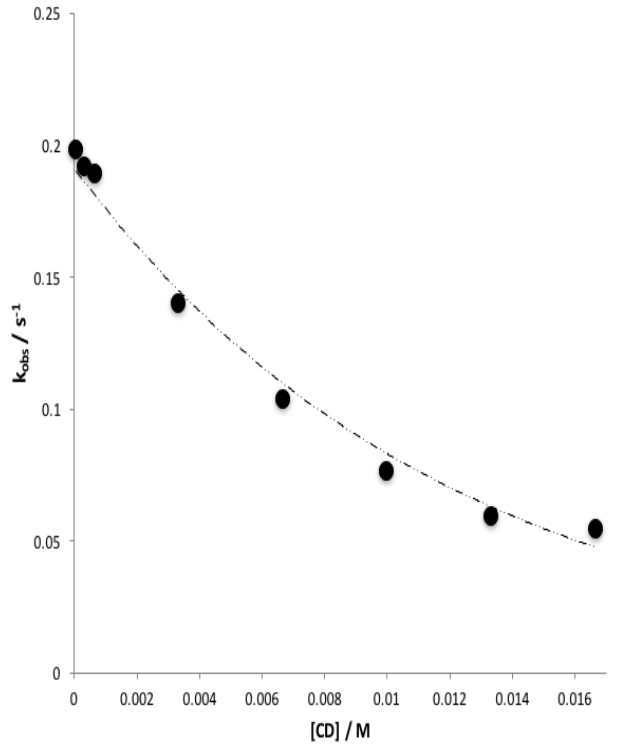
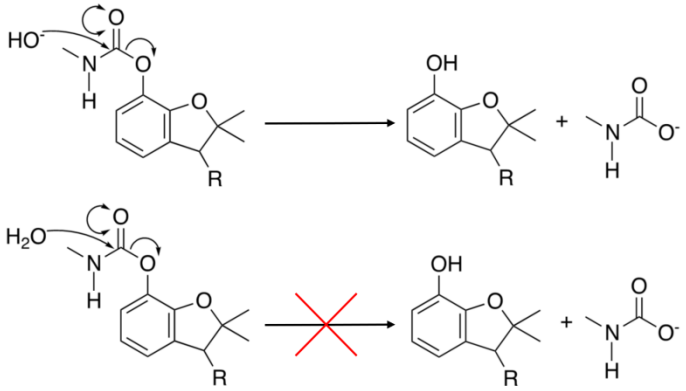


Figure 4: Influence of [β-CD] upon the basic hydrolysis of KCF (T=25ºC, [KCF]=8.33×10^{-5}M, [NaOH]= 1.00×10^{-3}M).

Discussion

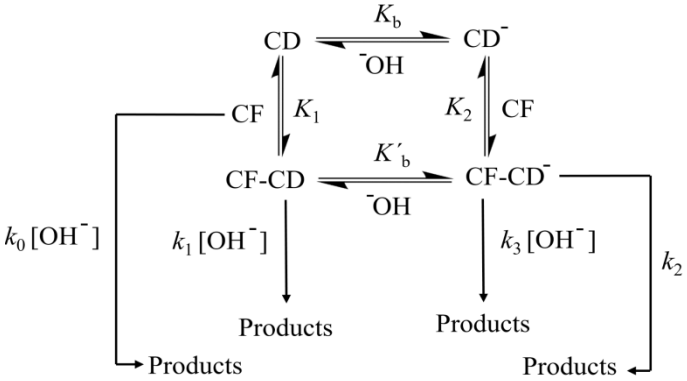
As quote above, the effects of β-CD on the basic hydrolysis of carbofuran-derivatives (KCF and HCK) with [NaOH] constant was carried out (figures 3-4). A clear non-linear decrease in the hydrolysis rate was found and this decrease reaches saturation in the reactivity of carbofuran which is related to host-guest complex formation between both carbamates and β-CD[24].

Also, we must emphasize that at [β-CD] constant and in presence of different values [HO^-] a linear relationship was found, where the absence of intercept implies that the basic hydrolysis goes through a nucleophilic attack of OH^- on the carbonyl group of the carbamate without the involvement of the water in the hydrolysis process[24] as scheme 4 shown.



Scheme 4: Reaction mechanism in the basic hydrolysis of carbofuran. R: -OH, HCF and R: =0, KCF.

Considering that the pK_a value for β-CD is 12.20 [24] the following kinetic model can be proposed (Scheme 5). According to this the following expression can be obtained for the observed rate constant (k_{obs}) (eq. 4).



Scheme 5: Kinetic model for the basic hydrolysis of carbofuran-derivatives in the presence of β-CD.

$$k_{obs} = \frac{k_0[HO^-]+k_1K_1[HO^-](1-f)[CD](k_2+k_3[HO^-])K_2f[CD]}{1+K_1(1-f)[CD]+K_2f[CD]} \quad (4)$$

where k_0, k_1 and k_3 are the hydrolysis rate constants of free substrate (KCF/HCF), the (KCF-CD/HCF-CD) complex and the (KCF-CD^-/HCF-CD^-) complex respectively; k_2 is the rate constant corresponding to the reaction of the CF with the CD^- once complexed. K_1 and K_2 are the inclusion constants. Finally, f is the ionized cyclodextrin fraction and it can be written as

$$f = \frac{[OH^-]}{[OH^-]+K_b} \quad (5)$$

To facilitate the fit of experimental data to eq. 4 experiments at different [β-CD] were carried out at [NaOH] concentrations for the limit values of fraction f which is f=0 and f=1[24]. The first conditions imply that the eq. 4 can be simplified by obtaining eq. 6 and the second conditions would allow to rewriting the eq. 4 as eq. 7:

$$k_{obs} = \frac{k_o[OH^-]+k_1K_1[OH^-][CD]}{(1+K_1)[CD]} \quad (6)$$

$$k_{obs} = \frac{k_o[OH^-]+(k_2+k_3[OH^-])K_2[CD]}{(1+K_2)[CD]} \quad (7)$$

Unfortunately, the errors in the kinetic coefficients and equilibrium constants taken from the fit of equations 6-7 to the experimental data do not allow a detailed analysis of them. Nevertheless, we can indicate that K_2, k_2, k_3 are negligible with respect to k_1[24] Finally,We can affirm that

The host-guest complex is unreactive, *ergo* β-CD hinder the access of hydroxyl ion to the carbonyl group of carbamates , and hence protecting them. This will be very helpful to understand carbofuran behaviour in the analytical, agro-environmental and food areas [26-29].

Conclusions

In summary, the inhibition of the hydrolysis process of the carbamates due to the encapsulation of them in the β-CD cavity implies a longer half-life of these xenobiotics. In this sense, the use of formulations consisting of the encapsulation of carbamates by β-CDs would allow, given their greater persistence, to reduce the concentration applied to the crops or the number of treatments needed during the growing season.

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