

Influence of Micelles on the Basic Degradation of Carbofuran

MANUEL ARIAS,[†] LUÍS GARCÍA-RÍO,[‡] JUAN C. MEJUTO,^{*,§}
 PEDRO RODRÍGUEZ-DAFONTE,[§] AND JESUS SIMAL-GÁNDARA[#]

Área de Edafología y Química Agrícola, Facultad de Ciencias de Ourense, Universidad de Vigo, Ourense, Spain; Departamento de Química física, Facultad de Química, Universidad de Santiago de Compostela, Santiago de Compostela, Spain; Departamento de Química física, Facultad de Ciencias de Ourense, Universidad de Vigo, Ourense, Spain; and Área de Nutrición y Bromatología, Facultad de Ciencias de Ourense, Universidad de Vigo, Ourense, Spain

The effect of micellar aggregates upon the stability of carbofuran in basic media has been studied. The effect of the presence of micelles upon the basic hydrolysis of carbofuran is a function of the nature of the surfactant monomer. Important catalysis of basic hydrolysis of carbofuran in the presence of colloid aggregates with positive surface charge has been reported. On the other hand, the presence of anionic and nonionic surfactants implies a large inhibition of the basic hydrolysis of carbofuran. Both catalysis and inhibition are due to the association of carbofuran with the micellar core. The kinetic constants for the basic hydrolysis of carbofuran in these microheterogeneous media have been obtained on the basis of a micellar pseudophase model. No significant changes in the intrinsic reactivity of HO⁻ against carbofuran have been observed.

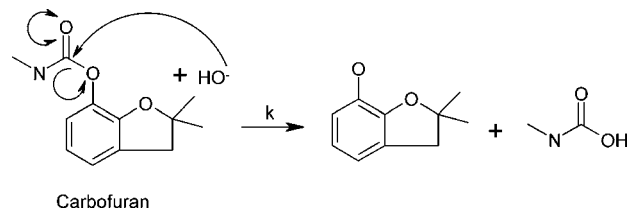
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INTRODUCTION

In the environment, pesticides degrade into a variety of other substances as a result of interactions with soil, water, sunlight, and oxygen (1). The presence and potential environmental effects of pesticide breakdown products are only now being included in environmental fate studies by the agencies responsible for monitoring concentrations of these compounds in the environment. When these breakdown products are monitored, they are commonly found in measurable quantities in water, sediments, and plant and animal tissues (2, 3). Living organisms also degrade pesticides. Soil microbes are responsible for catalyzing the breakdown of many pesticides, and in mammals, most pesticides are broken down in the liver to more soluble compounds, which are then excreted. Generally, pesticide breakdown products are less toxic than the pesticide itself. The rate of breakdown of a particular pesticide in the environment is a function of the pesticide, its location (whether it is adsorbed to soil or sediment particles, on an exposed leaf surface, in water, etc.), temperature, soil or water pH, and the moisture content of the surrounding medium.

Carbofuran, 2,3-dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate, is one of the carbamate pesticides (see **Scheme 1**), a large family of pesticides derived from carbamic acid. Carbofuran is used extensively in agriculture as an insecticide

Scheme 1



to control a broad spectrum of insects on corn, rice, alfalfa, grapes, and other foodstuffs. It is sprayed directly onto soil and plants just after emergence to control beetles, nematodes, and rootworm. The mechanism of action for carbofuran activity against insects is its rapid but reversible inhibition of acetylcholinesterase.

All carbamates and related products enter the ecosystem with potential adverse effects and recently their implications as potential endocrine disruptors have been demonstrated (4). Carbofuran is moderately persistent in soils with a half-life from 30 to 120 days depending on environmental conditions (such as the organic and moisture contents and pH of the soil); degradation occurs by exposure to sunlight to yield 2-hydroxyfuran and furadan phenol, by chemical hydrolysis and bioactivity. Carbofuran is highly mobile in soils and appears in the waters because of its high solubility (5, 6); it has a high potential for groundwater contamination of aquifers by leaching of treated fields, and it can also contaminate surface waters as a result of runoff from treated fields. Direct photolysis and photooxidation (via hydroxyl radical) is thought to be the major pathway to degradation of carbofuran in water. When compared

* Author to whom correspondence should be addressed (fax 34-988-387031; e-mail xmejuto@uvigo.es).

[†] Área de Edafología y Química Agrícola, Universidad de Vigo.

[‡] Universidad de Santiago de Compostela.

[§] Departamento de Química física, Universidad de Vigo.

[#] Área de Nutrición y Bromatología, Universidad de Vigo.

with other insecticides, carbofuran is less persistent than organochlorine, but it is more persistent than organophosphorus pesticides, the degradation of which has been studied in natural waters.

Surfactants, or amphiphiles, are surface-active nonionic molecules or organic salts that, either alone or in combination with a wide variety of other ionic and nonionic solutes, aggregate spontaneously and with a high degree of cooperativity in solution to form a variety of assemblies (or association colloids) whose structures depend both on solution composition and on the structures of the components, primarily the surfactant (7–9).

Micelles are highly dynamic, often polydisperse aggregates formed from single-chain surfactants (10) beyond the critical micelle concentration (cmc). Micellization is primarily driven by bulk hydrophobic interactions between the alkyl chains of the surfactant monomers and usually results from a favorable entropy change (11). The overall Gibbs energy of the aggregate for ionic surfactants (12) is a compromise of a complex set of interactions, with major contributions from headgroup repulsions and counterion binding. It has long been known that aqueous micelles can influence chemical reaction rates and equilibrium. Early studies of micellar effects on reaction rates and equilibrium are described in extensive monographs (7–9, 13–16). Much of the impetus for the study of reactions in micelles is that they model, to a limited extent, reactions in biological assemblies, and the term “biomimetic chemistry” has been coined to describe this general area of study.

Micellar catalysis of organic reactions has been extensively studied (17–23). This type of catalysis is critically determined by the ability of micelles to take up all kinds of molecules. The binding is generally driven by hydrophobic and electrostatic interactions. The uptake of solutes from the aqueous medium into the micelle is close to diffusion controlled, whereas the residence time depends on the structure of the surfactant molecule and the solubilize and is often of the order of 10^{-4} – 10^{-6} s (24). Solubilization is usually treated in terms of a pseudophase model in which the bulk aqueous phase is regarded as one phase and the micellar pseudophase as another. The time-averaged location of different solubilizes in or at a micelle has been a topic of contention (25). Apart from saturated hydrocarbons, there is usually a preference for binding in the interfacial region, that is, at the surface of the micelle (26, 27). Such binding locations offer possibilities for hydrophilic and hydrophobic interactions and avoid unfavorable disturbances of the interactions between the alkyl groups of the surfactant molecules in the core of the aggregate. The preferential binding of aromatic molecules at the micellar surface has been explained at least in part by the ability of the π -system of the molecule to form a weak hydrogen bond with water (28).

Our research group has carried out extensive studies about the influence on reactivity of micellar media (29, 30) and other colloidal aggregates (31–34). This paper presents a comparative study of carbofuran cleavage in the presence of anionic, cationic, and nonionic micellar aggregates.

MATERIALS AND METHODS

All reagents were Merck or Sigma-Aldrich products of the maximum commercially available purity, and none required further purification. All aqueous solutions were prepared by weight using double-distilled water.

Reaction kinetics was recorded at 25.0 ± 0.1 °C in a Kontron Uvicon 923 spectrophotometer equipped with thermostated cell carriers. The disappearance of the absorbance at 280 nm due to carbofuran consumption was followed. The initial concentration of carbofuran (1.94×10^{-5} M) was always much lower than that of the other reagents.

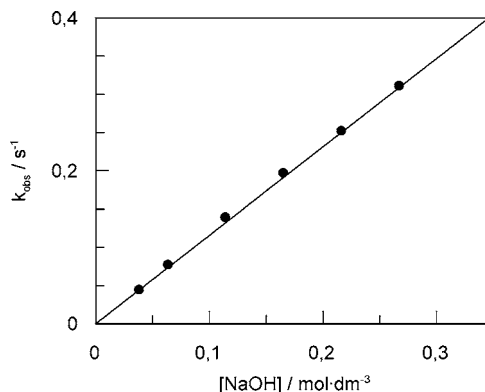


Figure 1. Influence of NaOH concentration upon pseudo-first-order rate constant of basic hydrolysis of carbofuran. [carbofuran] = 1.94×10^{-5} M. $T = 25$ °C.

The kinetic data always fitted the first-order integrated rate equation satisfactorily ($r > 0.999$; eq 1); in what follows, k_0 denotes the pseudo-first-order constant:

$$\ln(A_t - A_\infty) = \ln(A_0 - A_\infty) - k_0 t \quad (1)$$

where A_0 , A_t , and A_∞ are the absorbance at $t = 0$, at a given time, and at $t = \infty$, respectively.

In the case that the half-time life of the reaction was < 5 min, kinetics were recorded at Applied Photophysics DX17 MV sequential stopped-flow spectrophotometer thermostated at 25.0 ± 0.1 °C.

Critical micellar concentration values of nonionic surfactants have been obtained using surface tension measurements. The surface tension, $\sigma/m \text{ Nm}^{-1}$, was measured using a Kruss tensiometer (model K9) using the procedure of the Wilhelmy plate (35). Data were the averages of 10 measurements and exhibited deviations of $< 0.4\%$ in all instances. All of the measurements of surface tension had been carried out at 25.0 ± 0.1 °C.

Nonlinear regressions were carried out using Grafit 3.0 supplied by Erithacus Software Ltd.

RESULTS AND DISCUSSION

Basic Hydrolysis of Carbofuran in Water. Although the hydrolysis of aryl esters in aqueous media has been thoroughly studied, we examined the alkaline hydrolysis of carbofuran (36) to ensure good consistency in the evaluations of the experimental results. The mechanism of the cleavage reaction is shown in **Scheme 1**.

To determine the rate constant of basic hydrolysis of carbofuran in water the concentration of NaOH was varied between 3.8×10^{-2} and 0.3 M. The concentration of carbofuran was always 1.94×10^{-5} M in order to keep pseudo-first-order conditions as we describe under Materials and Methods.

Experimental results are shown in **Figure 1**. The kinetic equation for this reaction is $v = k_w[\text{NaOH}][\text{carbofuran}]$. In the pseudo-first-order conditions $k_0 = k_w[\text{NaOH}]$. The value of k_w has been obtained from the slope of the linear regression of k_0 versus [NaOH] (see **Figure 1**), and it was estimated in $k_w = 1.16 \pm 0.01 \text{ M}^{-1} \text{ s}^{-1}$.

Effects of Anionic Micelles. The effect of sodium decyl sulfate (SdS), sodium undecyl sulfate (SUS), and sodium dodecyl sulfate (SDS) on the basic hydrolysis of carbofuran was studied at $[\text{OH}^-]$ constant ($[\text{HO}^-]_{\text{total}} = 5.90 \times 10^{-3}$ M, $[\text{HO}^-]_{\text{total}} = 6.40 \times 10^{-3}$ M, and $[\text{HO}^-]_{\text{total}} = 6.70 \times 10^{-3}$ M for SdS, SUS, and SDS, respectively), and the concentrations of the different surfactants were varied typically between 0 and 0.12 M. **Figure 2** shows the pseudo-first-order rate constant, k_0 , to be markedly decreased by all of the anionic surfactants.

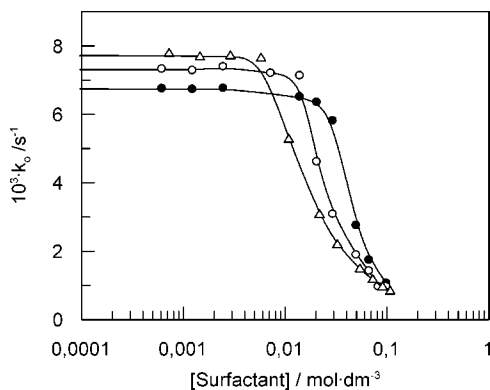
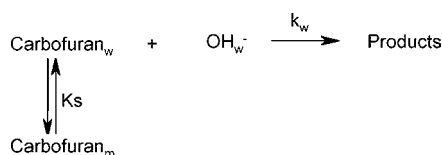


Figure 2. Influence of surfactant concentration upon pseudo-first-order rate constant of basic hydrolysis of carbofuran: (●) SdS micelles; (○) SUS micelles; (△) SDS micelles. Solid lines represent fit of eq 2 to the experimental data. [carbofuran] = 1.94×10^{-5} M. $T = 25$ °C.

Scheme 2



This behavior can be rationalized in terms of the two-pseudophase model (37–39) in which the reaction is assumed to occur both in micellar pseudophase and in water pseudophase, with an equilibrium distribution of carbofuran between the two pseudophases. On the basis of electrostatic considerations (40), the hydroxyl ions concentration at the micellar pseudophase must be very low owing to the anionic character of the micellar headgroup. This virtually complete exclusion of OH^- means that the reaction is taking place only in the aqueous pseudophase (see **Scheme 2**).

This model yields the following equation:

$$k_0 = \frac{k_w[\text{OH}^-]_w}{1 + K_s[\text{D}_n]} \quad (2)$$

In eq 2, $[\text{OH}^-]_w$ is the NaOH concentration in the bulk water that is approximately equal to the total NaOH concentration, k_w is the bimolecular rate constant in bulk water, K_s is the binding constant of the substrate to the micellar pseudophase $\{K_s = [\text{carbofuran}]_m / ([\text{carbofuran}]_w[\text{D}_n])\}$, and $[\text{D}_n]$ is the concentration of micellized surfactant ($[\text{D}_n] = [\text{surfactant}]_t - \text{cmc}$). The cmc values were obtained from the kinetic data and calculated as the minimum concentration of surfactant necessary to produce a change in the reaction rate. These values in the presence of OH^- are satisfactorily correlated with the expected behavior of cmc values when the length of the surfactant chain increases, which is a linear decrease in the logarithm of cmc with an increase in the number of carbons in the chain (41). The quality of the fit of the experimental data to eq 2 was satisfactory. In all cases the deviation was lower than 10% (see **Figure 3**). The kinetic coefficients for these systems are shown in **Table 1**.

The inhibitory efficiency of the different micelles increases with increasing chain length (6.5, 7.7, and 9.5 times-fold for SdSS, SUSS, and SDS, respectively). This inhibitory efficiency has been estimated as the ratio between the rate constant in water and the limit value of the kinetic constant in the presence of surfactant obtained using the pseudophase model equation. The observed trend is due to the increase of the K_s value on

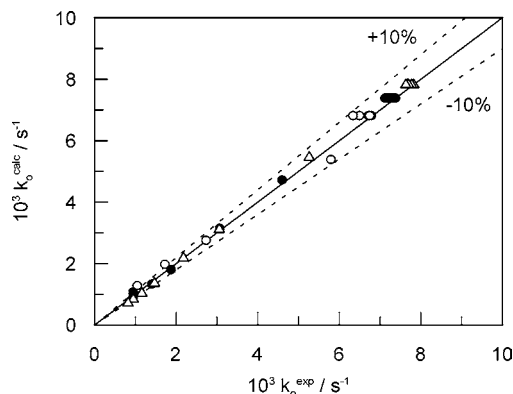


Figure 3. Experimental rate constant, k_0^{exp} , and calculated rate constant, k_0^{calc} (obtained from eq 2), for the basic hydrolysis of carbofuran in the presence of anionic micelles: (●) SdS micelles, (○) SUS micelles and (△) SDS micelles. $T = 25$ °C.

increasing the chain length of the surfactant. A higher value of K_s (63, 87, and 100) implies a larger value of inhibition. In fact, the ratio between inhibition and K_s value is almost constant, 9.7, 11.2, and 10.5 for SdS, SUS, and SDS, respectively.

Effects of Cationic Micelles. The effect of hexadecyl trimethylammonium bromide (CTABr), tetradecyl trimethylammonium bromide (TTABr), and dodecyl trimethylammonium bromide (LTABr) on the basic hydrolysis of carbofuran was studied at $[\text{OH}^-]_{\text{total}} = 1.0 \times 10^{-3}$ M, and the concentrations of the different surfactants were varied typically between 0 and 0.15 M. The results (**Figure 4**) follow the typical biphasic pattern. The reaction rates pass through a maximum as the surfactant concentration increases. The existence of a maximum can be explained in terms of two competing effects in the ion-exchange model. Added surfactant increases the relative concentration of carbofuran and HO^- in the Stern layer, which increases the reaction rate, and the ascending branch of the curve is observed. As the concentration of surfactant increases, the concentration of the reagents in the micellar pseudophase decreases, and furthermore the excess of unreactive counterions, X^- , competes with OH^- for available sites in the Stern layer, so that the reaction rate decreases. The relative contribution of these competing factors results in the experimental maximum. This experimental behavior can be explained quantitatively again on the basis of the pseudophase model. The overall reaction rate was, therefore, equal to the sum of the rates at the micellar and aqueous pseudophases (see **Scheme 3**).

Scheme 3 allows us to obtain the equation

$$k_0 = \frac{k_w[\text{OH}^-]_w + k_m K_s [\text{OH}^-]_m}{1 + K_s [\text{D}_n]} \quad (1)$$

from which we can obtain the equation

$$k_0 = \frac{k_w[\text{OH}^-]_{\text{total}} + (k_m K_s - k_w) m_{\text{OH}} [\text{D}_n]}{1 + K_s [\text{D}_n]} \quad (3)$$

where k_w is the bimolecular rate constant in bulk water, k_m is the rate constant in the micellar pseudophase, K_s $\{K_s = [\text{carbofuran}]_m / ([\text{carbofuran}]_w[\text{D}_n])\}$ is the binding constant of the substrate to the micellar pseudophase, $[\text{D}_n]$ is the concentration of micellized surfactant ($[\text{surfactant}]_t - \text{cmc}$), and m_{OH} denotes the $[\text{OH}^-]_m / [\text{D}_n]$ ratio, which satisfies the following equation

Table 1. Kinetic Coefficients for the Basic Hydrolysis of Carbofuran in the Presence of Anionic, Cationic, and Nonionic Micellar Aggregates, Obtained for the Application of the Pseudophase Model

surfactant	effect	$k_w/M^{-1} s^{-1}{}^a$	K_S	k_m/s^{-1}	$k_m^2/M^{-1} s^{-1}$
SdS, $CH_3(CH_2)_6CH_2OSO_3Na$	inhibition	1.16 ± 0.01	63 ± 4		
SUS, $CH_3(CH_2)_9CH_2OSO_3Na$	inhibition	1.16 ± 0.01	87 ± 3		
SDS, $CH_3(CH_2)_{10}CH_2OSO_3Na$	inhibition	1.16 ± 0.01	100 ± 3		
Brij-35, $C_{12}H_{25}(OCH_2CH_2)_{10}OH$	inhibition	1.16 ± 0.01	29 ± 1		
Brij-58 $C_{16}H_{33}(OCH_2CH_2)_{20}OH$	inhibition	1.16 ± 0.01	36 ± 1		
Brij-78, $C_{18}H_{37}(OCH_2CH_2)_{20}OH$	inhibition	1.16 ± 0.01	38 ± 1		
LTABr, $CH_3(CH_2)_{11}N(CH_3)_3Na$	catalsis	1.16 ± 0.01	20 ± 3	10.5 ± 0.6	1.47 ± 0.08
TTABr, $CH_3(CH_2)_{13}N(CH_3)_3Na$	catalsis	1.16 ± 0.01	48 ± 2	11 ± 1.0	1.5 ± 0.1
CTABr, $CH_3(CH_2)_{15}N(CH_3)_3Na$	catalsis	1.16 ± 0.01	52 ± 5	13 ± 2	1.8 ± 0.3

^a Value taken from the pure water experiments.

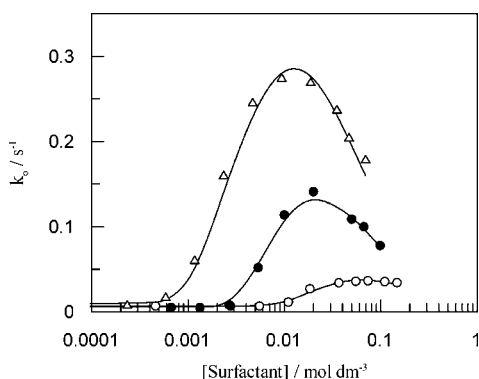
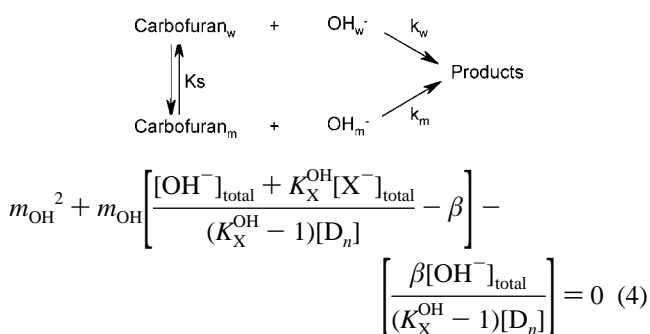


Figure 4. Influence of surfactant concentration on pseudo-first-order rate constant of basic hydrolysis of carbofuran: (●) TTABr micelles; (○) LTABr micelles; (△) CTABr micelles. [carbofuran] = 1.94×10^{-5} M. $T = 25$ °C.

Scheme 3



where $K_X^{\text{OH}} = \{K_X^{\text{OH}} = [\text{OH}^-]_w [\text{X}^-] / ([\text{OH}^-]_m [\text{X}^-]_w)\}$ is the ion-exchange constant, obtained from the influence of salts upon k_0 (see below). The cmc values were obtained from the kinetic data and calculated as the minimum concentration of surfactant necessary to induce a change in the reaction rate (see inset in **Figure 1**) and are listed in **Table 1**. β is the fraction of surfactant ions neutralized by counterions, which the ion-exchange pseudophase model assumes to be constant and independent of the concentration of surfactant (14, 16). The usual value of β is in the range of 0.6–0.9. We used $\beta = 0.8$ (16) as it seems to be the most frequently used value. Changes in β (in the range of 0.6–0.9) do not affect the fitting results. The good fit to the experimental data shows that the assumption of constant β is satisfactory and, in our case, independent of the nature of the

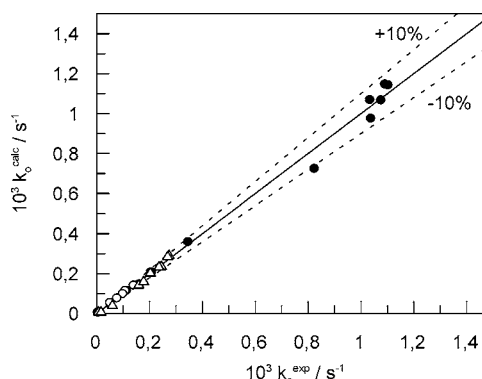


Figure 5. Experimental rate constant, k_0^{exptl} , and calculated rate constant, k_0^{calcd} (obtained from eqs 3 and 4), for the basic hydrolysis of carbofuran in the presence of cationic micelles: (●) TTABr micelles; (○) LTABr micelles; (△) CTABr micelles. $T = 25$ °C.

counterion. The subscripts m and w denote micellar and aqueous pseudophases, respectively.

The calculations were performed by means of a nonlinear fitting program based on Marquardt's algorithm. The fit was carried out using cmc values calculated from the kinetic data; k_w was the experimental value in bulk water, and K_S was obtained from the fitting of kinetic data for the acid hydrolysis to find the values of k_m and K_X^{OH} that best reproduce the kinetic data. The solid line in **Figure 4** represents the best fit of eqs 3 and 4 to the experimental data, using the value of K_X^{OH} obtained from the influence of salts upon the basic hydrolysis of carbofuran in the presence of cationic surfactants (30). This allows us to obtain again values of k_m in good agreement with those found in the study of the influence of salts. The values of K_X^{OH} are in accordance with the values reported in the literature (30, 42–45). The fitting results for different surfactants are shown in **Table 1**. The quality of the fit of the experimental data to pseudophase equations was satisfactory. In all cases the deviation was <10% (see **Figure 5**).

For comparing the reactivities in the micellar pseudophase with the corresponding reactivities in bulk water, k_m (defined in terms of moles per mole concentrations and expressed in s^{-1}) are converted into k_m^2 expressed in M. Using the well-known molar volume of the Stern layer ($\sim 0.14 \text{ mol}^{-1}$) (30), the k_m^2 values are compatible with the corresponding one in pure water. This fact implies that the catalytic effects observed are due to the increase in the local reagent concentration at the Stern layer. The kinetic coefficients for these systems are shown in **Table 1**.

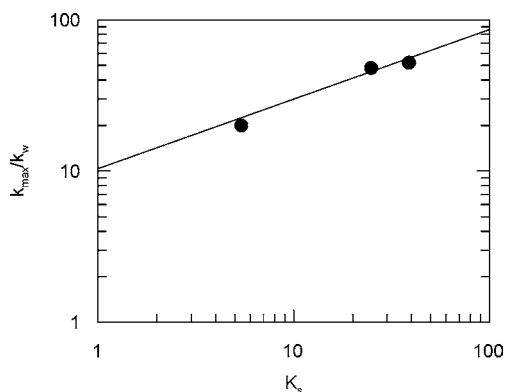


Figure 6. Linear relationship between the log/log plot of K_s and k_{\max}/k_w for cationic surfactants.

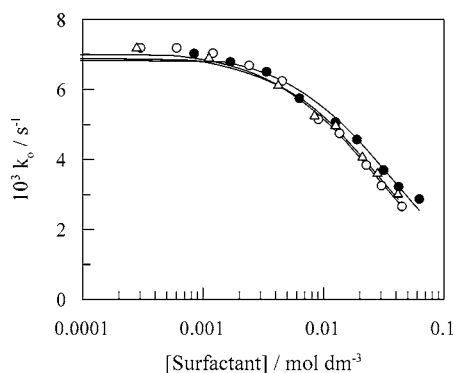


Figure 7. Influence of surfactant concentration on pseudo-first-order rate constant of basic hydrolysis of carbofuran: (●) Brij-35; (○) Brig-38; (△) Brij-78. [carbofuran] = 1.94×10^{-5} M. $T = 25$ °C. Solid lines represent fit of eq 5 to experimental data.

The catalytic efficiency of the different micelles (viz., k_{\max}/k_w) increases with increasing chain length (5.4, 24.9, and 39.8 for LTABr, TTABr, and CTABr, respectively). This trend 1:4.6:7.3 can be justified by taking into account the value of K_s (20, 48, and 52 for LTABr, TTABr, and CTABr, respectively). The relationship between the log/log plot of K_s versus k_{\max}/k_w is shown in **Figure 6**.

The pseudophase ion-exchange model is highly successful in explaining the results obtained for the alkaline hydrolysis of carbofuran in cationic micelles. It can also be addressed that hydrophobic forces drive the association of substrate with the micellar pseudophase and that the catalysis observed in these systems is not due to an intrinsically larger kinetic constant in the micellar pseudophase but to a local concentration effect. The relationship between the log/log plot of K_s versus k_{\max}/k_w is a good evidence of this fact.

Nonionic Micellar Effects on the Basic Hydrolysis of Carbofuran. The effect of Brij-35, Brij-58, and Brij-78 on the basic hydrolysis of carbofuran was studied at $[\text{OH}^-]$ constant ($[\text{OH}^-]_{\text{total}} = 6.20 \times 10^{-3}$ M), and the concentrations of the different surfactants were varied typically between 0 and 0.06 M (**Figure 7**), showing the pseudo-first-order rate constant, k_0 , to be markedly decreased by all of the nonionic surfactants.

This behavior can be rationalized in terms of the two-pseudophase model (37–39) in which the reaction is assumed to occur both in micellar pseudophase and in water pseudophase, with an equilibrium distribution of carbofuran between them. In the case of anionic surfactant, electrostatic considerations allow us to neglect the possibility of reaction in the micellar pseudophase because the hydroxyl ion concentration at the micellar pseudophase must be very low owing to the anionic

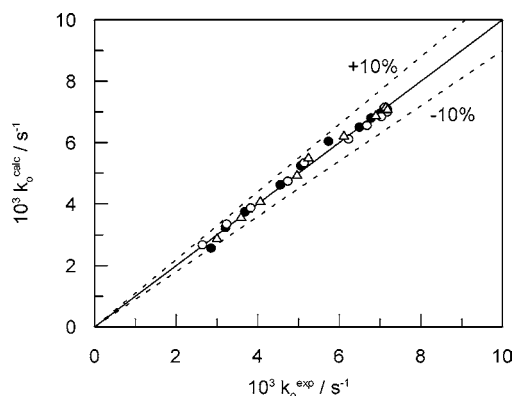


Figure 8. Experimental rate constant, k_0^{exptl} , and calculated rate constant, k_0^{calcd} (obtained from eq 5), for the basic hydrolysis of carbofuran in the presence of nonionic micelles: (●) Brij-35; (○) Brig-38; (△) Brij-78. $T = 25$ °C.

character of the micellar headgroup. In this case, the noncharged headgroups open the possibility that HO^- can be present in the micellar pseudophase, and hence, as in the case of cationic micelles, a second pathway of reaction can be expected (see **Scheme 3**).

Nevertheless, the experimental results show that the reaction in the micellar medium seems to be negligible against the reaction in the bulk water. For this reason, the behavior can be modeled using **Scheme 2**, which yields eq 2.

The quality of the fit of the experimental data to eq 2 was satisfactory. In all cases the deviation was $<10\%$ (see **Figure 8**). The kinetic coefficients for these systems are shown in **Table 1**.

The inhibitory effect of the different micelles is similar. This can be explained by taking into account that the K_s values of carbofuran for these three surfactants are almost the same (29 ± 1 , 36 ± 1 , and 38 ± 1 for Brij-35, Brij-58, and Brij-78, respectively).

To sum up, the effect of the presence of micelles upon the basic hydrolysis of carbofuran is a function of the nature of the surfactant monomer. Both anionic and nonionic surfactants inhibit the decomposition of carbofuran. However, the presence of cationic surfactants catalyzes the decomposition of carbofuran. Both catalysis and inhibition are due to the association of carbofuran to the micellar core. No significant changes in the intrinsic reactivity of HO^- against carbofuran have been observed. Changes in the apparent reactivity in the presence of micellar aggregates are attributed to the concentration of reagents in the micellar core (cationic surfactants) or the compartmentalization of reagents (electrostatic exclusion of HO^- of Stern layer and inclusion of carbofuran to the micellar core). Considering that the presence and concentration of the anionic surfactants in polluted waters is much larger than the other kind of surfactants (especially the cationic surfactants), the inhibitory effect observed is important for the persistence of the carbofuran pesticide in the presence of the anionic surfactants hindering its degradation.

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