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Reactivity differences of *O*-aryl *O*-(4-nitrophenyl) thionocarbonates versus their homolog carbonates: Micellar catalysis in hydrolysis reactions

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Abstract

The alkaline hydrolysis reaction of *O*-(4-cyanophenyl), *O*-(4-methylphenyl), and phenyl *O*-(4-nitrophenyl) thionocarbonates (**1**, **2**, and **3**, respectively) and *O*-(4-cyanophenyl) and phenyl *O*-(4-nitrophenyl) carbonates (**4** and **5**, respectively) has been spectrophotometrically studied in aqueous borate buffer media, in the presence of the cationic surfactant CTAB. The pseudophase model successfully explained the results obtained, in the presence of this cationic micelle, and various kinetic parameters were determined. Results show that the catalytic efficiency increases in carbonates and thionocarbonates. In fact, a catalytic efficiency (k_{obs}^{max}/k'_w) of 485-fold was found in the hydrolysis reaction of thionocarbonate **1**, while in the carbonate homolog **4**, the effect was of 146-fold. In addition, we found that at the same experimental conditions (Borate buffer pH = 9.0 and 25°C), an increase in the concentration of the buffer led to a decrease of the hydrolysis rate.

KEYWORDS

alkaline hydrolysis reaction, catalytic efficiency, micellar catalysis, thionocarbonate and carbonate reactivity

1 | INTRODUCTION

There is a great variety of organic reactions that are vital for our ecosystem, both biologically and industrially. That is why it becomes necessary to study and understand how these reactions happen, and then optimize them in the best way at the laboratory level. Among these reactions, one of the most important involves carbonyl and thiocarbonyl compounds,^[1] and it is relevant to understand their different reaction mechanisms to be able to establish working conditions that favor their synthesis or that help different transformations that lead to new compounds.

For example, the aminolysis reaction of thionocarbonates, which leads to the subsequent formation of thionocarbamates, is one of the most important reactions. Thionocarbamates possess a great number of biological actions, such as analgesics, anesthetics, fungicides, and bactericides.^[2] In addition, the hydrolysis of thionocarbonates, which is conducive to the formation of alcohols with their respective acid, is important. In this context, one of the most important reactions, based on the dissociation of thionocarbonates, is the Barton-McCombie reaction,^[3] whose objective is first to derivatize secondary and tertiary alcohols to thionocarbonates, and then to reduce them forming alkanes.

Moreover, changes caused by the micelles toward the medium generate alterations in the kinetics of the reactions,^[4] because these can change the local concentration of the substrates in the reaction medium, or also by the stabilization of substrates and intermediates affecting the reaction rate. This stabilization will depend on changes in charge of the reactants or the micelle. For example,

the same effect does not occur if it is an acid-base process, since the micelle could catalyze or inhibit it, depending on the type of micelle used.^[4b]

On the other hand, another important effect of the micelle in the medium is the hydrophobic effect, which causes catalytic effects in micellar systems to be accentuated when the substrate and its substituents possess greater hydrophobicity.^[5]

Several kinetic models^[6-8] have been developed to quantitatively analyze the kinetic effects in the presence of ionic surfactants.

The most frequently used model is the pseudo-phaseion-exchange (PIE), throughout the k_{obs} vs surfactant concentration profiles.^[6a,7] There are 2 important factors in the accelerations in surfactant solutions: (1) the interfacial ion exchange catalysis^[6–8] and (2) the large reagent concentrations in the small interfacial volume in which the reaction occurs.^[9]

The PIE model has been corrected when applied to nucleophilic substitution in buffered surfactant solutions, considering the competition of 3 anions in their micellar binding: the surfactant counterion, the buffer base, and the nucleophile.^[10]

On the other hand, the existence of catalytic or inhibition effects by micellar systems on the hydrolysis reaction of esters derivatives is well recognized. For example, Iglesias E.^[6d] reported that both cationic and nonionic micelles decrease the rate of the acid-catalyzed hydrolysis of the ester function of ethyl cyclohexanone-2-carboxylate. The author also found that keto ester associates strongly to cationic or nonionic micelles by hydrophobic interactions, such as the micellar interface.^[6c]

In this line, studies conducted by Al-Lohedan et al (2017) have demonstrated that the alkaline hydrolysis of carboxylate (1-naphthylbutyrate) and carbonate esters (2-(methylsulfonyl)-ethyl-4-nitrophenylcarbonate) is enhanced in the presence of cationic micelles of cetyltrimethylammonium (CTA) bromide and CTA sulfate and inhibited by anionic micelles of sodium dodecyl sulfate.^[11] Recent studies by Hojo et al^[12] have reported that the hydrolysis reactions of *p*-nitrophenyl benzoate in the presence of cationic surfactants, such as CTAB or CTAC, lead to an increment in the rate constant values of 140-fold and 200-fold for CTAB and CTAC, respectively. Whereas, the anionic surfactant, sodium dodecyl sulfate, has caused only a gradual rate deceleration by the same reaction.^[12]

Thus, taking into account the catalytic effect that cationic micelles would have on reactions of hydrolysis of carbonyl compounds, it is interesting to assess the micellar effect on such reactions in a series of thionocarbonates and their homolog carbonates. To this end, in the present work, a kinetic study of the hydrolysis reaction toward 4cyanophenyl, phenyl and 4-methylphenyl 4-nitrophenyl

$$\begin{array}{c} X \\ H \\ 0_2 N - & - 0 - C - 0 - & - Y \\ 1.- X=S, Y=CN \\ 2.- X=S, Y=H \\ 3.- X=S, Y=CH_3 \\ 4.- X=O, Y=CN \\ 5- X=O, Y=H \end{array}$$

SCHEME 1 Structures of the studied thionocarbonates and carbonates compounds

thionocarbonates (1, 2, and 3, respectively; Scheme 1), and 4-cyanophenyl and phenyl 4-nitrophenyl carbonate (4 and 5, respectively; Scheme 1) in the presence of increasing concentrations of CTAB was carried out.

2 | EXPERIMENTAL

2.1 | Material

Thionocarbonates **1** to **3** and carbonate **5** were prepared as described.^[13] The carbonate **4** was prepared as in the Supporting Information.

The surfactant hexadecyltrimethylammonium bromide (CTAB, 99%) was supplied by Sigma-Aldrich. Solutions were freshly prepared before use and stored refrigerated for no more than 2 days.

Merck supplied all other reagents, and the solutions were prepared with doubly distilled water obtained from a permanganate solution.

Substrates in acetonitrile solutions, buffer, and CTAB solutions were prepared daily by dilution of the stock solution. The percentage of organic solvent in the working solution was less than 2% by volume.

2.2 | Product analysis

In both the absence or presence of surfactant, 4-nitrophenyl aryl thionocarbonates **1** to **3** and of 4-nitrophenyl aryl carbonate **4** to **5** hydrolysis yield 4-nitrophenolate ion. The absorption spectra of the studied reactions in basic media present a band centered at 400 nm that increases with time because of the formation of 4-nitrophenolate ion.

2.3 | Kinetic measurements

The kinetics of the hydrolysis reactions of substrates **1** to **5** are analyzed through a diode array spectrophotometer, at $25.0 \pm 0.1^{\circ}$ C. The reactions were followed in the 250 to 500 nm wavelength range, with the initial concentration of the substrate being in the range of 2 to 8×10^{-5} M. This concentration range enables following the reaction by recording the absorbance of 4-nitrophenolate ion.

Because of the low solubility of substrates, in water and in lower CTAB concentrations, their concentrations are in a range near 2×10^{-5} M. pH was maintained constant by using borate as the external buffer. Under these conditions, pseudo-first-order rate coefficients (k_{obs}) were found throughout, the kinetics being measured for at least 5 half-lives at 400 nm. The experimental conditions and the k_{obs} values obtained for the studied reactions are summarized in Tables S1 to S7 in the Supporting Information.

3 | RESULTS AND DISCUSSION

3.1 | Hydrolysis reactions of thionocarbonates and carbonates in the absence of surfactant

Pseudo-first-order rate constant (k_{obs}) in the absence of CTAB at different NaOH concentrations, by following the absorbance at 400 nm, were determined (Tables S1 and S2 in the Supporting Information). Plots of k_{obs} against the hydroxide concentrations obey Equation 1, where k_0 and k_w are the rate constants for hydrolysis by water and hydroxide ion, respectively. The obtained k_w values are summarized in Table 1.

$$k_{\rm obs} = k_0 + k_{\rm w}[\rm OH] \tag{1}$$

The comparison between the hydrolysis rate constant in the reactions of carbonates **4** and **5** shows that k_w are approximately 40 and 180 times faster than those of thionocarbonates **1** and **2**, respectively. There are at least 3 reasons to explain these results:

- The above results have been explained in a destabilization of the tetrahedral intermediate because of the greater ability of O⁻ than S⁻ in the intermediate to form the double bond with the central carbon and expel both the leaving group and the nucleophile. This is because of the stronger pi-bond energy of the C—O group (by 40 kcal mol⁻¹) relative to C—S.^[14]
- This difference in the hydrolysis rate constant is because of the different electrophilicity of the carbon atom present on the carbonyl with respect to the carbon atom of the thiocarbonyl, since in the case of the

TABLE 1Hydrolysis rate constants for the hydrolysis reactions ofsubstrates (1-5) in the absence of CTAB

Substrate	$k_{\rm w}$, s ⁻¹ M ⁻¹	n	R^2
1	3.32 ± 0.03	10	0.999
2	0.18 ± 0.01	5	0.977
3	0.31 ± 0.01	5	0.989
4	146 ± 5	5	0.995
5	33 ± 1	4	0.997

thiocarbonyl, it is more polarizable. This causes a greater positive charge on the carbon of the C—O double bond compared to the C—S double bond.^[14b]

• On the other hand, the nucleophile, in this case hydroxide ion, corresponds to a hard nucleophile, so it has greater affinity with a carbonyl bond than a thiocarbonyl bond.

Similarly, the comparison between the hydrolysis rate constant of thionocarbonates and carbonates studied (see Table 1) shows the effect of the nonleaving group. In fact, while greater is the electron withdrawing of this group, more electrophilic is the thiocarbonyl group and therefore greater hydrolysis rate constants.

3.2 | Hydrolysis reactions of thionocarbonates and carbonates in the presence of surfactant

The pseudo-first-order rate constant increases in the presence of a small amount of surfactant above the critical micelle concentration (cmc) until it reaches a maximum; after this point, an increase in surfactant concentration diminishes the observed rate constant (see Figures 1–3). This behavior is explained considering the micelle formation, the amount of substrate in the micelles, the competition between OH⁻, borate and the increasing amount of Br⁻, and the dilution of the substrate in the micelles.^[12]

These studies have suggested strongly that in micellar media, most reactions take place on the surface of micelle at or near the highly charged double layer, commonly called the *Stern layer*.



FIGURE 1 k_{obs} vs CTAB concentration profile in the hydrolysis reaction of **1**, (a) pH = 9.13; (b) pH = 9.05, borate buffer 20 mM; and (c) pH = 9.0, buffer Borate 40 mM, at 25° C. Points are experimental values (Table S3 in the Supporting Information) and the curves were calculated with Equations 2 to 7 and values of Table 2.

3.2.1 | Hydrolysis reactions of aryl thionocarbonates

Thionocarbonate **1** hydrolysis reactions were studied spectrophotometrically in the presence of a variable amount of CTAB near pH = 9.0 in 2 different borate buffer concentrations; the experimental conditions and k_{obs} values found are summarized in Table S3 in the Supporting Information. Figure 1 shows the k_{obs} vs [CTAB] profiles of these reactions.

There are two observations from Figure 1:

- 1. The results show that in curves **a** and **b** (also in Table S3 in the Supporting Information), only 0.08 pH units in difference lead to changes of 11% in k_{obs} values; as a consequence of different total OH⁻.
- 2. The corresponding curves **b** and **c** (in Table S3 in the Supporting Information) show kinetic differences; in fact, part of the decrease in k_{obs} is obvious because of the decrease in pH (0.05 pH units), but most of the decrease is because of the increased concentration of the buffer. This is also a consequence of the ion exchange equilibrium.^[10b]

It was initially stated that borate anion does not bind $CTA^{[12]}$; nevertheless, the micellar effect found is strong evidence for a binding of borate anion. Probably, even the borate anion binds micelles weakly, its high concentration (20-40 mM), relative to the total [OH⁻] (~10⁻⁵ M), allows its participation in the pseudo phase and therefore in the kinetic.

The pseudo-first-order rate constants obtained of the hydrolysis reactions of thionocarbonates **2** and **3** at different CTAB concentrations are in Tables S4 and S5 in the Supporting Information. Figure 2 shows the k_{obs} against [CTAB] profiles for these reactions.

It can be observed that for each concentration of CTAB, the values of k_{obs} of **2** and **3** hydrolysis reactions are similar between them, and lower than those of **1**, although **2** and **3** compounds are measured at a higher pH. The great difference with the hydrolysis of **1** can, in principle, be attributed to the same reasons discussed in relation with the same reactions in water solution (vide supra), although differences in the association of substrates with micelle cannot be ruled out.

3.2.2 | Hydrolysis reactions of aryl 4-nitrophenyl carbonates

Carbonates **4** and **5** hydrolysis reactions were studied spectrophotometrically in the presence of a variable amount of CTAB at pH = 8.3 and pH = 9.0, respectively, and 20 mM borate buffer; experimental conditions



FIGURE 2 k_{obs} vs [CTAB] profiles of the hydrolysis reactions of (A) *O*-phenyl *O*-(4-nitrophenyl) thionocarbonate **2** at pH 9.53 and (B) of *O*-(4-methylphenyl) *O*-(4-nitrophenyl) thionocarbonate **3** at pH 9.60 in both in the presence of 20 mM borate buffer, at 25°C. Points are experimental values (Tables S4 and S5 in the Supporting Information), and curves were calculated with Equations 2 to 7 and values of Table 2.

and k_{obs} values found are summarized in Tables S6 and S7 in the Supporting Information. These results are shown in Figure 3.

As in aqueous solutions, the k_{obs} for the hydrolysis reactions of the carbonyl derivatives are greater than those of thiocarbonyl. The comparison of the corresponding curves in Figures 1–3 clearly shows that the k_{obs} values for the hydrolysis reactions of the diarylcarbonates **4** and **5** are greater than those of **1** and **2**, respectively, although the carbonates are carried out at minor pH.



FIGURE 3 k_{obs} vs CTAB concentration profile in the hydrolysis reaction of (A) **4** at pH = 8.3 and (B) **5** at pH = 9.0; in both [borate buffer] = 20 mM, at 25°C. Points are experimental values (Tables S6 and S7 in the Supporting Information), and curves were calculated with Equations 2 to 7 and values of Table 2.

These can be because of the different hydrophobicity and/ or the different electrophilicity of substrates, and will be discussed later (see below).

In addition, as in the thionocarbonate series, the reactions of carbonates **4** and **5** clearly show the influence of the nonleaving group in the substrates. This behavior is because of the differences in solubility in the micelles and/or differences in the electrophilicity of the electrophilic group in the substrates.^[6]

3.2.3 | Quantitative kinetic study for the hydrolysis reactions of aryl-thionocarbonates and carbonates in CTAB

With the aim to do a quantitative kinetic study for these reactions, the PIE model^[6a,7a] was applied. Scheme 2 shows this model, which consider the partition substrate between the water (S_w) and the micelle (S_m) with an equilibrium constant (K_{ass}) and 2 parallel reactions that lead to the same product; k_w' and k_m' are the pseudo-first-order rate constants and $D_n = ([surfactant total] - cmc)$. In the tested systems, S_w represents the carbonate or thionocarbonate derivatives, and the micellized surfactant (D_n) used is CTAB.

The rate equation deduced for this model is (Equation 2):

$$k_{\rm obs} = \frac{k'_{\rm w} + k'_{\rm m} K_{\rm ass}[D_{\rm n}]}{1 + K_{\rm ass}[D_{\rm n}]}$$
(2)

The pseudo-first-order rate constants k'_{w} and k'_{m} are related to the second-order rate constants by equations

$$k'_{\rm w} = k_{\rm w} * [\rm OH^-]_{\rm w} \tag{3}$$

$$k'_{\rm m} = k_{\rm m} * [{\rm OH}^-]_{\rm m}$$
 (4)

Substitution in Equation 2 lead to Equation 5 where m_{OH} is the concentration ratio of hydroxyl ion in the micellar pseudo phase, $m_{\text{OH}} = [\text{OH}]_{\text{m}}/[D_{\text{n}}]$

$$k_{\rm obs} = \frac{k_{\rm w} [{\rm OH}^-]_T + (k_{\rm m} K_{\rm ass} - k_{\rm w}) [D_{\rm n}] m_{\rm OH}}{1 + K_{\rm ass} [D_{\rm n}]} \qquad (5)$$

Because we observe an important dependence of $k_{\rm obs}$ with the buffer concentration in this study, we use the



SCHEME 2 Equilibrium and hydrolysis reaction step of the substrates **1-5** in CTAB micelles

model of Scheme 2, Equation 5; but the $m_{\text{OH}-}$ values were calculated by Equation 6, which consider the ionic interchange of the 3 counter ions in the micelle.^[10a,15a]

$$m_{OH}^{3}(1-K_{OH^{-}/buffer})(1-K_{OH^{-}/Br^{-}}) + m_{OH}^{2}[A_{1}(1-K_{OH^{-}/buffer}) + (1-K_{OH^{-}/Br^{-}}) \\ ([OH]_{T}K_{OH^{-}/buffer} + [buffer]_{T})] + m_{OH}[OH]_{T} \\ [K_{OH^{-}/Br^{-}}([buffer]_{T} - (1-\alpha)[D_{n}](1-K_{OH^{-}/buffer})) \\ + K_{OH^{-}/buffer}A_{1}] - K_{OH^{-}/Br^{-}}(1-\alpha)[D_{n}]K_{OH^{-}/buffer}[OH^{-}]_{T}^{2} = 0$$
(6)

In this equation, the terms $K_{\text{OH}^-/\text{Br}^-}$ and $K_{\text{OH}^-/\text{buffer}}$ correspond to the ion exchange constant, α corresponds to the degree of ionization of individual micellar species, while parameter A_1 is defined according to Equation 7.

$$A_{1} = \alpha [D_{n}] + CMC + K_{OH^{-}/Br^{-}}[OH]_{T}$$

+ $(1-\alpha)[D_{n}]K_{OH^{-}/Br^{-}}$ (7)

Equation 6 was solved numerically by the Newton-Raphson method. Table 2 summarizes the $k'_{\rm m}$ and $K_{\rm ass}$ obtained from the adjustment of the experimental results with those obtained in the PIE model. In adjustments of Equation 4, cmc = 0.0005 M (determined in this study), $\alpha = 0.28$, and for the interfacial ion exchange constant ($K_{\rm OH^-/Br^-}$,) the value 0.048 described by Sepulveda et al^[16] was used as fixed parameters. For $K_{\rm OH^-/buffer}$, the best values was 15.5 in all the reactions, except for the reactions of **1** in [borate buffer] = 40 mM, where the best value was 7.75.

Comparison between entries 1 to 3 in Table 2 shows that, as expected, there are not differences in the $k'_{\rm m}$ and $K_{\rm ass}$ values, showing that the differences observed in Figure 1 are only a consequence of the experimental conditions.

About the change of thiocarbonyl by carbonyl in the 4-cyanophenyl derivatives **1** and **4**, the value of $k'_{\rm m}$ is about 30 times greater for **4** (entries 1 and 6 in Table 2).

TABLE 2 Values of K_{ass} and k'_{m} by fitting of the kinetics profiles of Figures 1–3 with the pseudo-phase-ion-exchange model

Entry	Substrate	рН	[Borate], mM	k'_{m} , s ⁻¹	$K_{\rm ass},{ m M}^{-1}$
1	1	9.05	20	53 ± 1	1550 ± 70
2	1	9.13	20	51 ± 1	1440 ± 70
3	1	9.00	40	45 ± 1	1500 ± 100
4	2	9.53	20	0.19 ± 0.04	3100 ± 200
5	3	9.60	20	0.15 ± 0.03	3100 ± 200
6	4	8.30	20	1480 ± 50	540 ± 40
7	5	9.00	20	88 ± 2	680 ± 30

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Likewise, comparison between the phenyl derivatives **2** and **5** (entries 4 and 7 in Table 2) shows that a $k'_{\rm m}$ is 460 times greater for the carbonyl derivative. On the other hand, the value of the equilibrium constant of association $K_{\rm ass}$ is greater for **1** and **2** than **4** and **5**, respectively, probably because of their differences in hydrophobicity.

Related to the nonleaving group's effects, it is concluded that as the hydrophobicity increases, high K_{ass} values were obtained ($3 \sim 2 > 1$; Table 2). For comparative purpose of the carbonate series, a K_{ass} value (~200) for the hydrolysis reaction of bis(4-nitrophenyl) carbonate, reported by other authors, has been considered.^[5b] In view of the latter, we observed the same tendency for the carbonates series, phenyl > 4-cyanophenyl > 4-nitrophenyl.

The comparisons between the results of Table 2 suggest that in the micellar effects, both the association of substrate to the micelle and the nucleophilic substitution reaction go in different directions.

The micellar effects can be analyzed from the quotient between the hydrolysis rate constant in the bulk (k_w) and the maximum value obtained in the presence of the surfactant (k_{obs}^{max}) .^[10b] Considering that both terms are dependent on the experimental conditions, to conduct a more trustworthy comparison, we calculate these values at the same pH and borate concentration. Table 3 shows the micelle effects in the studied reactions.

The effect on hydrolysis reactions of thionocarbonate **1** is about 3 times greater than that of the carbonate **4**. Undoubtedly, these results may be because of the higher concentration of thionocarbonate in the micellar pseudo-phase derived from its higher constant association equilibrium; however, a possible catalytic effect in the hydrolysis step cannot be ruled out. On the contrary, the effect is 1.5 times greater for the carbonate **5** than thionocarbonate **2**, in spite of the latter presenting a greater K_{ass} .

In both series, it can be observed that the maximal effect is on the 4-cyano derivative, which presents the minor K_{ass} , reinforcing the idea that both factors (association in the micelles and catalytic process) are important.

TABLE 3 Kinetics parameters obtained for the hydrolysis reac-tions of substrates 1-5

	Substrate				
Kinetic Parameters	1	2	3	4	5
$10^4 k'_{\rm w} (s^{-1})^{\rm a}$	0.33	0.018	0.031	14.6	3.27
$10^4 k_{\rm obs}^{\rm max} \ ({\rm s}^{-1})^{\rm a}$	160	0.55	0.485	2140	160
$k_{ m obs}^{ m max}/k'_{ m w}$	485	31	16	146	49
k_{2m} , s ⁻¹ M ⁻¹	7.4	0.0266	0.0212	207	12.3
$k_{\rm 2m}/k_w$	2.1	0.141	0.0682	1.42	0.373

^aCalculated with the values of Table 2, at pH = 9.0 and [borate] = 20 mM.

It is not possible to directly compare the values of k_w (Table 1) with those of k_m (Table 2) because they are defined in different units.^[8b] To convert them to the same units (s⁻¹ M⁻¹), it is common to multiply k'_m by the molar volume of the Stern layer to obtain the term k_{2m} corresponding to the micellar constant in units of second order. A generally accepted value of molar volume of the Stern layer is 0.14 1 mol⁻¹.^[6c,9] Table 3 summarize the k_{2m} values obtained.

For the hydrolysis reaction of thionocarbonate **1** and carbonate **4**, the k_{2m}/k_w ratio is greater than 1, suggesting that there is a catalytic effect; therefore, the acceleration observed in the micelle is due to both an increment of the local concentration of substrate in the micelle and by a catalytic effect. On the other hand, the values of k_{2m}/k_w are clearly minor than 1 for the thionocarbonates **2** and **3** and carbonate **5**, suggesting an inhibiting effect, and therefore, the observed accelerations are only because of the increase of the local concentration of substrates in the micelle. In summary, substrates containing the 4-cyanophenyl as nonleaving group (**1** and **4**) present catalytic effect whereas those with phenyl (**2** and **5**) or 4-methylphenyl (**3**) as nonleaving groups present inhibition.

4 | CONCLUSIONS

- The pseudophase ion exchange model is highly successful in explaining kinetics results obtained for the hydrolysis of substrates **1** to **5** in CTAB, considering the ionic interchange of three anions in the micelle interphase (OH⁻, Br⁻, and borate).
- The catalytic efficiency increases from carbonate 4 to thionocarbonate 1; a k^{max}_{obs}/k'_w ratio of 485 times was found in the hydrolysis reaction of thionocarbonate 1, while in the carbonate homolog 4, the effect was 146 times.
- It is possible to conclude that the micellar effect on the hydrolysis reaction of thionocarbonate 1 and carbonate 4 is favored for both greater solubility (*K*_{ass}) and catalytic effect (*k*_{2m}/*k*_w).
- For the hydrolysis reaction of thionocarbonates 2 and 3 and of carbonate 5, the acceleration observed in the micellar medium is only because of the concentration of substrate in the micelle.
- Substrates with 4-cyanophenyl as nonleaving group (1 and 4) present catalytic effect, whereas those with phenyl (2 and 5) or 4-methylphenyl (3) as nonleaving groups present inhibition.
- The *K*_{ass} values between thionocarbonates **1** or **2** and CTAB micelles are about 3 times higher than those determined by their homologs **4** and **5** because of the greater hydrophobicity of the thiocarbonyl group than carbonyl.

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SUPPORTING INFORMATION

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