

Influence of Colloid Suspensions of Humic Acids on the Alkaline Hydrolysis of N-Methyl-N-Nitroso-*p*-Toluene Sulfonamide

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ABSTRACT: The influence of humic substances (HSs) upon the alkaline hydrolysis of N-methyl-N-nitroso-*p*-toluene sulfonamide has been studied. Important inhibition of hydrolysis reaction has been reported. This inhibition has been explained in terms of association of reactants to the humic substances. Kinetic results have been modeled using the micellar pseudophase model. © 2010 Wiley Periodicals, Inc. *Int J Chem Kinet* 42: 316–322, 2010

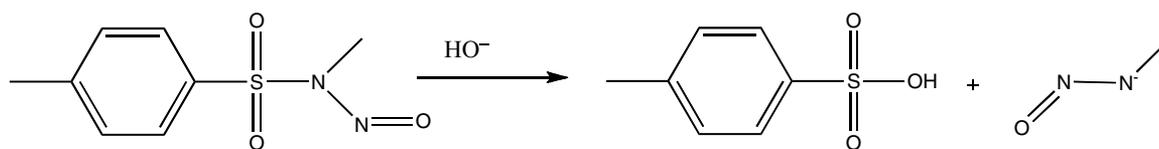
INTRODUCTION

Humic substances (HSs) make up a large portion of the organic matter found in natural environments with a typical concentration ranging from 0.1 to 200 mg L⁻¹ dissolved organic carbon [1]. HSs are anionic poly-electrolytes that represent 65%–75% of the total organic matter in soils. Average molecular weight ranges from 2 to 400 kDa, depending on the determination method [2]. An empirical formula for the basic structure of humic acids (HSs) has been proposed [3]: C₇₂H_{43–95}O₃₀N₄·0–38H₂O. They are characterized spectroscopically by a strong band of aliphatic

absorption (C–H) between 2980 and 2920 cm⁻¹ and other two bands at 1720 and 1650 cm⁻¹ due to the presence of carbonyl and carboxyl groups. The specific surface of humic substances is around 900 m² g⁻¹, and their negative surface charge presents a large dependence with pH (surface charge increases on increasing pH). This surface charge is mainly due to the deprotonation of carboxyl and phenol groups (they both represent 85%–90% of the surface charge of humic aggregates) [1]. The presence of amino groups may justify the presence of positive charges in the humic surfaces but as compared with the negative charges due to carboxyl and phenol groups, it is negligible. Fully ionized the capacity of cationic interchange (CIC) is 0.3–0.6 mol₍₊₎ kg⁻¹.

HSs can complex many environmental pollutants [4,5]. In particular, they are able to complex heavy metals [6–8] (due to the presence of –COOH and

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Scheme 1

—OH groups in their molecules) and persistent organic xenobiotics [9] (due to the presence of hydrophobic structures in their molecules), but also strongly interact with mineral surfaces [10]. The interaction of HSs with xenobiotics may modify the uptake and toxicity of these compounds by living organisms and affect the fate of pollutants in the environment. If traditionally HSs have been considered as inert, nowadays many aspects of their reactivity have changed our understanding about their role in environmental processes and rather they are now considered as reactive carriers, influencing fluxes of substances. At the same time the reactivity of HS has been comparatively little analyzed, although HSs contain many groups and structures that in similar macromolecules are responsible for their catalytic activity [11,12]. This question is of particular importance, because the main factor responsible for removal of organic xenobiotics (pesticides, PCBs, PAHs, and many other substances) is commonly thought to be microorganisms, neglecting the role of HSs. Among properties of HSs possibly influencing their catalytic activity is their ability to form micelles [13]. There are few studies in which the catalytic activity of HSs has been compared [11,12,14–19]. At the same time the study of the catalytic activity of HSs may be very important, considering their possible role in the fate in biogeochemical cycling of elements and high concentrations of HSs in natural environments. The velocity of different reactions could be influenced by the presence of HSs [11,12,14–19]. Reactions of interest would be related to hydroxyl ion attack, much studied to evaluate micellar catalysis [20,21]. In fact, it is well known that hydrolysis processes are among the major transformation pathways for numerous xenobiotics such as pesticides or pharmaceuticals in the environment [19–21].

The nitrososulfonamides have been demonstrated to be very efficient nitrosating agents [22], with 1a *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (MNTS) being one of the compounds of major interest [23]. The acid and basic hydrolysis mechanism, as well as the transnitrosation processes that involve MNTS, has been previously studied in our laboratory in an aqueous medium and microheterogeneous media [24–29]. For these reasons, the reaction becomes a useful one for

studying the chemical reactivity of colloids and other microorganized media.

The basic hydrolysis mechanism is shown in Scheme 1. This reaction is typically a “well-behaved” one and has become an interesting source of information on the role of the different factors that affect overall reactivity in micelles of HSs (i.e., compartmentalization of the reagents and characteristics of the humic aggregate as reaction medium). The aim of the present work was to study the catalytic activity of HSs in mentioned reactions and its rationalization in the bases of the pseudophase model for micellar catalysis.

EXPERIMENTAL

Reactives

All reagents (MNTS and NaOH) were Sigma-Aldrich (Madrid, Spain) products of the maximum commercially available purity and were used without further purification.

HSs used in this study were isolated from soil using the method described elsewhere [30]. The composition of the HSs used was determined by CNH elemental analysis using a Fisons EA-1108 elemental analyzer (518 g kg⁻¹ C, 40 g kg⁻¹ N, and 40 g kg⁻¹ H). Its ash content was 61 g kg⁻¹. HS functional group distribution has been determined by the Schinitzer methods [31]. The functional group distribution was total acidity 5.99 mol kg⁻¹, COOH groups 3.30 mol kg⁻¹, and total OH groups 2.91 mol kg⁻¹.

All aqueous solutions were prepared by weight using double-distilled degasified water.

Kinetic Measurements and Data Analysis

The kinetic procedures largely conformed to well-established practices [32]. Reactions were monitored through the first-order acid or basic hydrolysis of MNTS at 250 nm, using a Kontron Uvikon 923 spectrophotometer with the observation cell thermostated at (25.0 ± 0.1)°C.

All kinetic tests were conducted under pseudo-first-order conditions ([MNTS] = 1.56 × 10⁻⁵ M ≪ [OH⁻]). The integrated first-order rate law was fitted to the absorbance–time data by linear regression in all cases (*r* > .999; Eq. (1)); in what follows, *k*_{obs} denotes

the pseudo-first-order constant and A_i , A_t , and A_∞ are the absorbance at $t = 0$, at a given time, and at $t = \infty$, respectively.

$$\ln(A_t - A_\infty) = \ln(A_i - A_\infty) - k_{\text{obs}}t \quad (1)$$

The observed rate constants, k_{obs} , were thus reproduced to within $\pm 3\%$. In each instance, it was observed that the final spectrum of the product of the reaction coincided with the one obtained in pure water, guaranteeing that the presence of HS micelles would not alter the product of the reaction. Because HSs absorb in the UV-vis region, the spectrum of HSs in the absence of reaction was used as blank.

Nonlinear regressions were carried out using Grafit 5.0 supplied by Erithacus Software Ltd.

RESULTS AND DISCUSSION

Although the hydrolysis of MNTS in homogeneous media has been thoroughly studied [33], we examined the basic hydrolysis of MNTS to ensure good consistency in the evaluations of the experimental results. The rate constant for the basic hydrolysis of MNTS in aqueous medium is $k_w = (4.79 \pm 0.07) \text{ M}^{-1} \text{ min}^{-1}$. This result is in good concordance with the literature [34].

The influence of humic aggregates on the alkaline hydrolysis of MNTS has been studied. The concentration of HSs was varied between 0 and 24 mg L^{-1} . To minimize the possible consumption of NaOH by the humic substance, for each concentration of HSs the influence of NaOH concentration on the basic hydrolysis of MNTS was investigated ($[\text{NaOH}] = 0.01, 0.02, 0.03 \text{ M}$) to obtain the apparent bimolecular rate constant ($k_{2,\text{app}}$). Figure 1 shows, as an example, the deter-

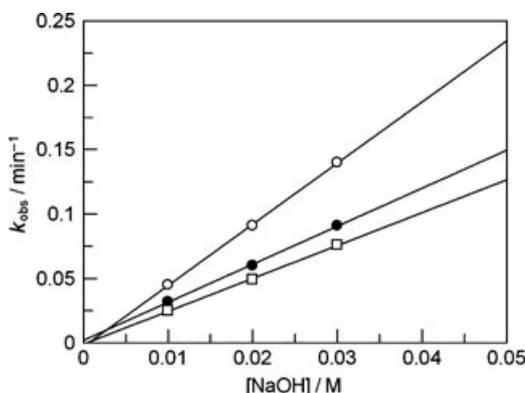


Figure 1 Influence of the pseudo-first order rate constant (k_{obs}) on the basic hydrolysis of MNTS in the presence of HSs. (○) $[\text{HS}] = 1.0 \text{ mg/L}$, (●) $[\text{HS}] = 10.0 \text{ mg/L}$, and (□) $[\text{HS}] = 24.0 \text{ mg/L}$.

Table I Influence of HS Concentration upon the Apparent Bimolecular Rate Constant for the Basic Hydrolysis of MNTS in the Presence of HSs

$[\text{HS}]$ (mg L^{-1})	$k_{2,\text{app}}$ ($\text{M}^{-1} \text{ min}^{-1}$)	$[\text{HS}]$ (mg L^{-1})	$k_{2,\text{app}}$ ($\text{M}^{-1} \text{ min}^{-1}$)
1	4.5 ± 0.1	12	2.9 ± 0.2
2	4.4 ± 0.2	14	2.8 ± 0.1
3	4.3 ± 0.3	16	2.7 ± 0.1
4	4.0 ± 0.1	18	2.7 ± 0.1
5	3.9 ± 0.3	20	2.6 ± 0.1
6	3.6 ± 0.1	22	2.5 ± 0.1
8	3.5 ± 0.2	24	2.5 ± 0.1
10	3.2 ± 0.1		

mination of the apparent bimolecular rate for three different HS concentrations. NaOH concentration values imply that all humic acid would be as sodium humate. Table I shows the obtained values for $k_{2,\text{app}}$.

As we can see in Table I and Fig. 2, the value of the apparent bimolecular rate constant ($k_{2,\text{app}}$) for the basic hydrolysis of MNTS decreases on increasing the HS concentrations. Hence, the presence of HSs inhibits the basic hydrolysis of MNTS.

The presence of HSs implies an inhibition of two times the hydrolysis rate. This inhibition is due to the association of MNTS to the HS substances, and it can be explained in terms of the pseudophase model [35–37].

In HS dispersions the loci of a reaction could be located in one or more of the following environments: (i) the HS aggregate or (ii) the bulk solvent. The nature of the HS aggregate, like the interior of a micelle, formed by the hydrophobic portion of the HSs, is not fully understood. But, taking into account the knowledge about micelles, the center of the HS aggregate

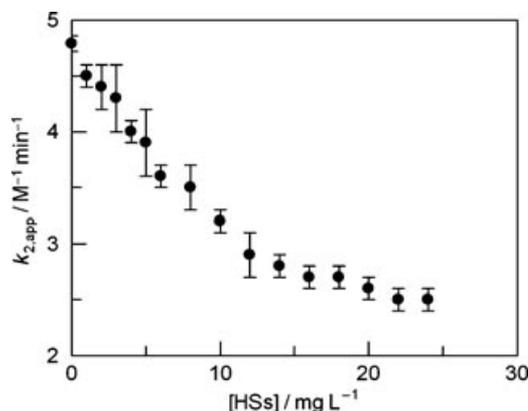


Figure 2 Influence of apparent bimolecular rate constant ($k_{2,\text{app}}$) on the basic hydrolysis of MNTS in the presence of HSs.

would be similar to liquid hydrocarbon, and water can penetrate the aggregate, so that part of the hydrocarbon chains of HSs from the hydrophilic groups would be exposed to the water. In this way, if our molecule is adsorbed in the very inner part of a micelle, it would be inert to hydroxide ion. This fact is due to the anionic nucleophile, which is certainly absent in the hydrocarbon. Electrostatic considerations, taking into account the negative surface charge of HSs, can justify the absence of HO^- from the vicinity of an HS aggregate. Whereas, in the case that HO^- can approximate the HS aggregate, we must take into consideration the fact that HS is a very compact unit; most of the interior water will be highly structured, and in these conditions it is well known that basic hydrolysis would be markedly impeded, and it could result in a total inhibition of the reaction [38–42].

The other possibility is that the MNTS is not adsorbed by the HS aggregates and exists only in the free water, but this possibility would imply the absence of an HS concentration effect upon the hydrolysis rate.

The rate inhibition observed in Fig. 2 may be explained by MNTS adsorption into the hydrocarbon center of the aggregate where presumably there is no anionic nucleophile (HO^-) or into the outer aqueous areas of the aggregate where the hydroxide ion concentration might be greatly reduced because of electrostatic factors originating at the HS surface. But the absence of a total inhibition upon reaction would also prove that the reaction occurs in the bulk water.

Taking into account all these considerations, we propose the reaction as shown in Scheme 2.

Assuming that all HS molecules are involved in the formation of aggregates, hence, K_s can be defined as

$$K_s = \frac{[\text{MNTS}]_m}{[\text{HSs}][\text{MNTS}]_w} \quad (2)$$

where $[\text{MNTS}]_m$ and $[\text{MNTS}]_w$ are, respectively, the concentrations of MNTS in both pseudophases (water pseudophase and micellar pseudophase). According to

Scheme 2, we can write the kinetic equation as

$$k_0 = k_w[\text{MNTS}]_w[\text{HO}^-]_w \quad (3)$$

where k_0 is the pseudo-first order rate constant and k_w is the bimolecular rate constant at the bulk water, in the presence of HSs.

On the other hand, HO^- is excluded from the Stern layer and from the core of the aggregate; hence, its concentration in water would be the total concentration of HO^- added. Also, the concentration of MNTS can be written as

$$[\text{MNTS}]_t = [\text{MNTS}]_w + [\text{MNTS}]_m \quad (4)$$

Using Eq. (2), the concentration of MNTS in water can be written as a function of the total MNTS concentration and the K_s (Eq. (2))

$$[\text{MNTS}]_t = [\text{MNTS}]_w + K_s[\text{HSs}][\text{MNTS}]_w \quad (5)$$

$$[\text{MNTS}]_w = \frac{[\text{MNTS}]_t}{1 + K_s[\text{HSs}]} \quad (6)$$

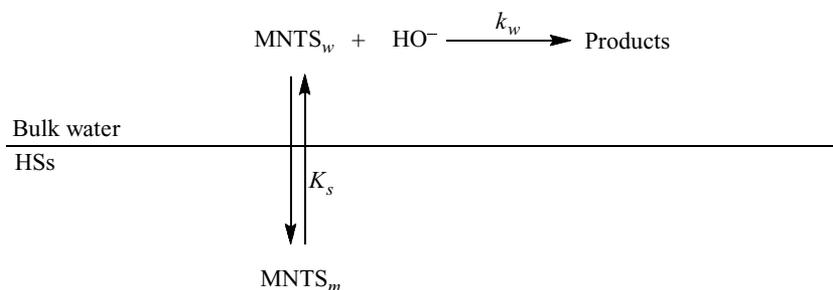
Taking into account Eqs. (3) and (6), we can write

$$k_0 = \frac{k_w[\text{HO}^-]_t}{1 + K_s[\text{HSs}]} \quad (7)$$

As quoted above, to minimize the possible consumption of NaOH by the humic substance, for each concentration of HSs the influence of NaOH concentration on the basic hydrolysis of the MNTS pseudo-first-order rate constant has been obtained. The apparent bimolecular rate constant ($k_{2,\text{app}}$) has been obtained as the slope of the linear fit shown in Fig. 1 (k_0 vs. $[\text{HO}^-]_t$). Then, Eq. (3) can be written as a function of $k_{2,\text{app}}$ instead of k_0 :

$$k_0 = k_{2,\text{app}}[\text{HO}^-]_t \quad (8)$$

$$k_{2,\text{app}} = \frac{k_w}{1 + K_s[\text{HSs}]} \quad (9)$$



Scheme 2

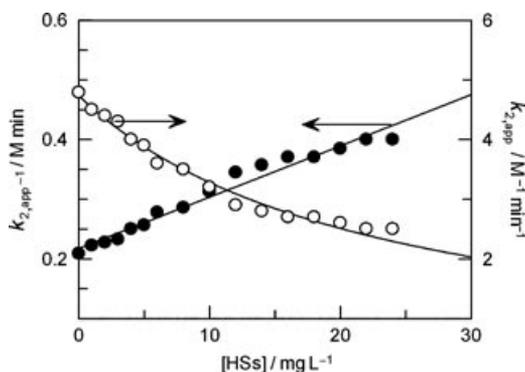


Figure 3 Influence of apparent bimolecular rate constant ($k_{2,app}$) on the basic hydrolysis of MNTS in the presence of HSs. Solid lines represent the fit of the experimental data to Eq. (9) (○) and to Eq. (10) (●)

This equation can be easily linearized as

$$\frac{1}{k_{2,app}} = \frac{1}{k_w} + \frac{K_s}{k_w} [\text{HSs}] \quad (10)$$

The values of k_w used for the experimental data (Table I) fitted to Eqs. (9) and (10) were the corresponding ones in bulk water (vide supra). The quality of the fit of the experimental data (Figs. 3 and 4) to Eqs. (9) and (10) was satisfactory.

The binding constant of MNTS to the HSs was $K_s = (25 \pm 2) \text{ mg}^{-1} \text{ L}$. However, because of the units of this binding constant, we are not able to compare directly this value with the corresponding ones for normal micellar aggregates to evaluate the hydrophobicity of the HS core.

Recently in our research group, the influence of HS aggregates upon alkaline fading of stable triarylmethyl

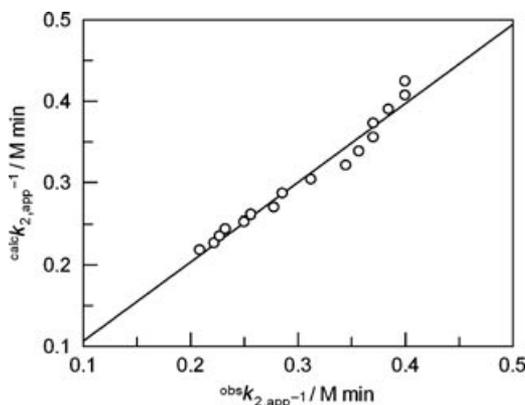


Figure 4 Experimental values and calculated values (Eq. (10)) for the apparent bimolecular rate constant ($k_{2,app}^{-1}$) for the basic hydrolysis of MNTS in the presence of HSs.

carbocations (crystal violet, CV, and malachite green, MG) provided a useful tool to compare the HS aggregates with traditional micelles [14]. These reactions have a long chemical tradition. The rate for the process, in spite of being a cation–anion combination, is slow enough for a conventional kinetic study, and in fact, the reaction has become a popular one for undergraduate laboratories [43]. The reaction also takes place with nucleophiles other than OH^- , a fact that has been used for the construction of the familiar Ritchie N_+ nucleophilicity scale [44]. In spite of the many studies made of the mechanism of these reactions, some mechanistic essential details are still unclear and the reaction has become one of the main challenges to the reactivity-selectivity principle [45,46].

The reaction has also become a useful one for studying chemical reactivity in organized media. In fact, one [47] of the first studies on micellar catalysis and inhibition referred to the alkaline fading of CV, and these reactions were later used very often for studies in normal micelles and other self-assembly colloids [48–51]. The reaction is typically a “well-behaved” one and has become an interesting source of information on the role of the different factors that affect overall reactivity in normal micelles (i.e., compartmentalization of the reagents and characteristics of the micellar reaction medium). In Fig. 5, we show the ratio between the binding constants of MNTS and CV values to each normal micelle. The insert of Fig. 5 presents the values of the binding constants of MNTS [28,37,39–41] and CV [42,52] for different normal micelles as a function of the chain length of the surfactant. Taking into account these ratios, and assuming that the binding constant of

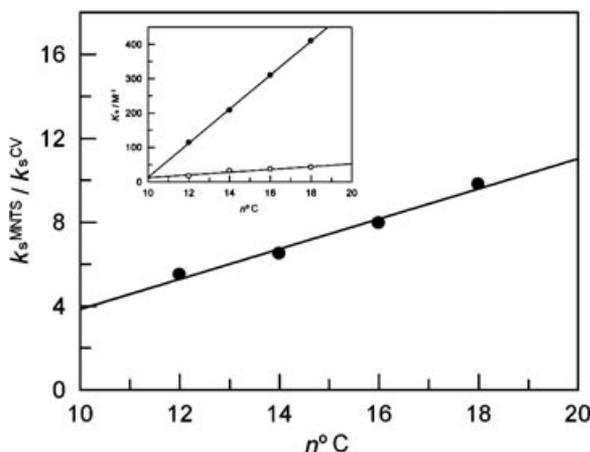


Figure 5 Value of the ratio between the binding constants of MNTS and CV to each normal micelle. The insert corresponds to the values of the binding constants of MNTS and CV for different normal micelles as a function of the chain length of the surfactant.

CV [15] to HSs is $K_s = 0.13 \text{ mg}^{-1} \text{ L}$, the value of $K_s^{\text{MNTS}}/K_s^{\text{CV}}$ is equal to 192. This value is 19 times bigger than the ratio $K_s^{\text{MNTS}}/K_s^{\text{CV}}$ for OTACI and 45 times bigger than the ratio of SDS. This means that the hydrophobicity of the HS core is significantly bigger than the corresponding one of normal micelles.

To sum up, the kinetic effect of the presence of HSs can be modeled using the pseudophase model. The HSs are colloid dispersions in water, and their influence on chemical reactivity can be rationalized considering that HSs are micelle-like colloids.

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