

# Chemical Reactivity in AOT Microemulsions: Kinetics of Water Replacement in a Square-Planar Palladium(II) Aquo Complex by Monoalkylthioureas

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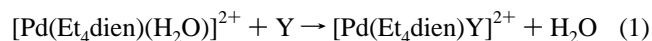
The kinetics of water replacement in the cationic palladium(II) aquo complex  $[\text{Pd}(\text{Et}_4\text{dien})(\text{H}_2\text{O})]^{2+}$ , where  $\text{Et}_4\text{dien} = \text{Et}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NEt}_2$ , by thiourea, methylthiourea, and ethylthiourea have been studied at 25.0 °C in heptane–AOT–water microemulsion over a wide range of the molar ratio  $R (= [\text{H}_2\text{O}]/[\text{AOT}])$  at the constant surfactant concentration of 0.13 mol dm<sup>-3</sup>. The reaction rates are significantly higher in microemulsions than in bulk water and decrease rapidly as the parameter  $R$  increases. The kinetic data, interpreted quantitatively by applying the pseudophase model to the microemulsion, indicate that there is a weak partitioning of the nucleophiles between the water core and the AOT interface, while the palladium complex is strongly associated with the negatively charged surfactant interface. All the substitution reactions take place only in the AOT interfacial region with rates very close to those in bulk water. The estimated partition coefficients of the nucleophiles increase with increasing their hydrophobic character. These data are discussed and compared with those previously obtained in the presence of cationic and anionic micelles.

## Introduction

Water-in-oil (w/o) microemulsions,<sup>1</sup> formed by liquid mixtures of water, oil (organic solvent), and a suitable surfactant, are heterogeneous on a microscopic scale and consist of spherical water droplets in a continuous oil phase separated and stabilized by a monolayer of the surfactant molecules. Sodium bis(2-ethylhexyl) sulfosuccinate (AOT), forming a negatively charged interface, is the most commonly used and studied surfactant that is capable of stabilizing the w/o microemulsions without having to add a fourth component (a cosurfactant). The sizes of the microemulsion droplets can be varied by changing the molar water/surfactant ratio  $R (= [\text{H}_2\text{O}]/[\text{AOT}])$ .

Since the microemulsion droplets can be considered as particular microreactors, large interest in these systems arises from their use as suitable reaction media,<sup>2–10</sup> in which chemical equilibria and reaction rates may be greatly altered as compared with conventional solvents. For their peculiar characteristics the microemulsions have found a growing number of scientific and technological applications, such as in polymerization, extraction, and purification processes, stereoselective synthesis, and photochemical and enzymocatalytic reactions, in food and nutrition science.

In our laboratory we have previously studied the kinetics of reaction 1 involving the water replacement in the cationic palladium(II) complex  $[\text{Pd}(\text{Et}_4\text{dien})(\text{H}_2\text{O})]^{2+}$ , where  $\text{Et}_4\text{dien} = \text{Et}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NEt}_2$ , by some alkyl-substituted thioureas



(Y) in water and in the presence of cationic<sup>11</sup> and anionic hydrocarbon<sup>11,12</sup> and perfluorocarbon<sup>12</sup> micelle-forming surfactants, the binding constants of the nucleophilic ligands being estimated from the kinetic data. The rates of the reaction 1 using as entering ligands the anions  $\text{S}_2\text{O}_3^{2-}$  and  $\text{SCN}^-$  have

been also measured<sup>13</sup> in the presence of anionic micelles of the surfactant sodium dodecyl sulfate (SDS). All these substitution reactions occur by an associative mechanism.<sup>11–13</sup> We have now extended the kinetic investigation of the reaction 1 to AOT-stabilized w/o microemulsions using as nucleophile thiourea (Tu), methylthiourea (Me–Tu), and ethylthiourea (Et–Tu) exhibiting different hydrophobic and steric character brought about by the alkyl substituents. The rate measurements have been carried out at 25.0 °C in heptane–AOT–water microemulsions over a wide  $R$  range ( $4 \leq R \leq 30$ ) at the fixed surfactant concentration of 0.13 mol dm<sup>-3</sup>, the concentration being based on the whole volume of solution. The present kinetic study, apart from our interest in obtaining information on the reactivity of inorganic reactions in microemulsion systems, allows the comparison of the various kinetic results obtained in different organized surfactant assemblies.

## Experimental Section

The surfactant AOT (Sigma) was dried for some days under vacuum to remove water. Heptane (Fluka) was used without further purification. The complex  $[\text{Pd}(\text{Et}_4\text{dien})(\text{H}_2\text{O})](\text{NO}_3)_2$  was prepared as described elsewhere.<sup>11</sup> Alkyl-substituted thioureas (Aldrich) were the substances purified and used previously.<sup>11,12</sup> Water was doubly distilled from alkaline permanganate solution.

For rate experiments a microemulsion containing the complex and a second microemulsion containing a given nucleophile at the desired  $R$  and  $[\text{AOT}]$  values were obtained by adding appropriate aliquots of aqueous solutions of the two reactants (and water, when necessary) to a standard organic solution of AOT. To avoid formation of hydroxo species from the palladium complex, the pH of its aqueous solution was adjusted<sup>11</sup> to about 4 by addition of  $\text{HNO}_3$ . The organic AOT solution was prepared daily to avoid ester hydrolysis. The two microemulsions, prepared before use, were then mixed in a HI-TECH SF-61 stopped-flow or a Beckman DU-7 HS spectrophotometer

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**TABLE 1: Experimental,  $k$ , and Calculated,  $k(\text{calc})$ ,<sup>a</sup> Second-Order Rate Constants ( $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ ) for Substitution Reaction 1 in Heptane–AOT–Water Microemulsions at Constant  $[\text{AOT}] (=0.13 \text{ mol dm}^{-3})$  and Varying  $R$  Values ( $t = 25.0^\circ \text{C}$ )**

$R$	Tu <sup>b</sup>		Me–Tu <sup>b</sup>		Et–Tu <sup>b</sup>	
	$k$	$k(\text{calc})$	$k$	$k(\text{calc})$	$k$	$k(\text{calc})$
4.0	32.1	30.3	36	35	30.5	30.3
5.0	27.4	26.8	32.0	31.6	28.6	28.9
7.0	20.8	21.7	27.1	27.1	26.2	26.3
9.0	18.3	18.2	23.1	23.7	24.0	24.1
12.0	14.7	14.7	19.6	19.9	21.5	21.4
15.0	12.1	12.3	16.8	17.2	19.3	19.3
20.0	9.6	9.7	14.6	14.0	16.6	16.6
25.0	8.2	8.0	11.7	11.8	14.5	14.5
30.0	6.8	6.8	10.2	10.2	12.9	12.9

<sup>a</sup> Calculated by using eq 6 and the data of Table 2. <sup>b</sup>  $k_{\text{aq}} = 1.87$ , 2.28, and  $2.95 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$  at  $\mu = 0.03 \text{ mol dm}^{-3}$  for Tu, Me–Tu, and Et–Tu, respectively.<sup>11</sup>

to follow the reaction rate. Both apparatus were equipped with thermostated compartments and interfaced to a computer for all data collection and analysis. All reactions were studied under pseudo-first-order conditions with nucleophile concentration ( $=5.0 \times 10^{-3} \text{ mol dm}^{-3}$ ) larger than the concentration ( $=5.0 \times 10^{-5} \text{ mol dm}^{-3}$ ) of the palladium complex. The rates of disappearance of the complex were followed at the wavelength of 300 nm. Other experimental details have been given previously.<sup>7,9</sup> The observed pseudo-first-order rate constants,  $k_{\text{obs}}$ , were reproducible to within  $\pm 3\%$ . According to previous<sup>11,12</sup> findings, the second-order rate constants,  $k$ , were calculated by the ratios  $k_{\text{obs}}/[\text{Y}]$ .

The temperature of the experiments was  $25.0 \pm 0.1^\circ \text{C}$ . The concentration values reported in this work refer to the whole volume of microemulsion, unless otherwise indicated.

## Results and Discussion

The estimated second-order rate constants  $k$  for the substitution reactions examined in heptane–AOT–water microemulsions of various compositions are reported in Table 1 together with the second-order rate constants  $k_{\text{aq}}$  obtained previously<sup>11</sup> for the corresponding reactions in homogeneous aqueous solution. The kinetics have been studied at the fixed AOT concentration of  $0.13 \text{ mol dm}^{-3}$  by changing the parameter  $R$  over the range 4–30. It is possible to observe that all the reactions are significantly faster in microemulsions than in bulk water and that the reaction rates decrease rapidly as the water droplet size (i.e., the parameter  $R$ ) increases.

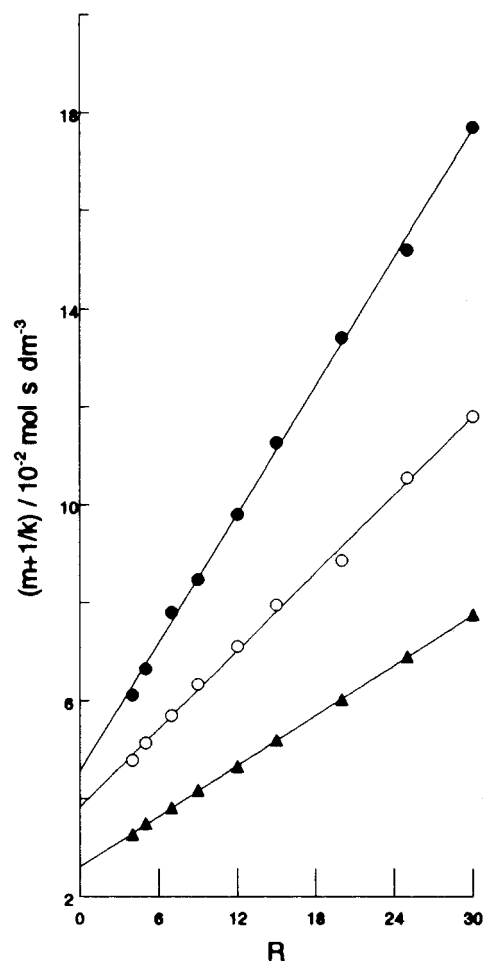
The kinetic results obtained can be quantitatively explained by applying the pseudophase model<sup>3–6,8–16</sup> generally used for reactions in micellar systems. The microemulsions are assumed to be divided into three regions corresponding to the oil-rich domain (o), the central aqueous core (w), and the surfactant interfacial region (s). The volume fractions of these pseudophases can be estimated<sup>5,9,15</sup> by expressions 2–4, where 0.018 is the

$$\phi_w = 0.018 [\text{AOT}] R \quad (2)$$

$$\phi_s = V [\text{AOT}] \quad (3)$$

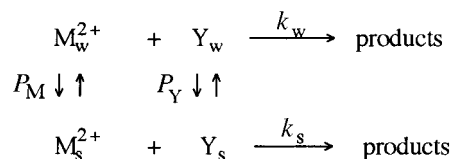
$$\phi_o = 1 - (\phi_w + \phi_s) \quad (4)$$

molar volume of water and  $V$  may be considered either the molar volume<sup>15</sup> of AOT ( $V = 0.390 \text{ dm}^3 \text{mol}^{-1}$ ) or an “effective” pseudo-phase volume<sup>3</sup> (per mole of surfactant) in which reaction occurs.



**Figure 1.** Plot of  $1/k$  against  $R$  in heptane–AOT–water microemulsions for Tu ( $m = 3$ ) (●), Me–Tu ( $m = 2$ ) (○), and Et–Tu ( $m = 0$ ) (▲).

## SCHEME 1



A bimolecular reaction leading to the (not reversible) formation of the products, like the substitution reaction of the present study, with the two reactants partitioned between the aqueous core and the interface (and, then, in the absence of a pathway that takes place in the organic phase and of an appreciable contribution of partitioning of species between oil and other phases) is expected, in the most general case, to occur according to the Scheme 1. In this reaction scheme  $\text{M}^{2+}$  represents the palladium complex and  $P_M (= [\text{M}^{2+}]_s / [\text{M}^{2+}]_w)$  and  $P_Y (= [\text{Y}]_s / [\text{Y}]_w)$ , are the dimensionless partition coefficients of the given species between the two pseudophases indicated by the subscript (local concentrations in each phase are used in  $P_M$  and  $P_Y$ ). In the case of the cationic palladium complex the  $\text{Na}^+$  counterion competition<sup>10,11,16</sup> for sites at the AOT surface might also be taken into account, but, as will be seen later, this is uninfluential in this study.

It can be derived<sup>4,9</sup> that, under the pseudo-first-order conditions used ( $[\text{Y}] \gg [\text{M}^{2+}]$ ), the reported reaction scheme implies that the second-order rate constant  $k$  depends on the microemulsion composition according to eq 5. It should be noted

**TABLE 2: Kinetic Parameters and Partitions Coefficients ( $P_Y$ ) of Monosubstituted Thioureas in Heptane–AOT–Water Microemulsion and Partition Coefficients ( $P_X$ ) Obtained in Cationic and Anionic Micelles ( $t = 25.0$  °C)**

	Tu	Me–Tu	Et–Tu	Bu–Tu <sup>a</sup>
$(k_s/V)^b/s^{-1}$	$8.4 \pm 0.5$	$7.1 \pm 0.3$	$4.98 \pm 0.02$	
$k_s P_Y^b/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$0.53 \pm 0.01$	$0.88 \pm 0.02$	$1.37 \pm 0.01$	
$VP_Y^b/\text{dm}^3 \text{ mol}^{-1}$	$0.063 \pm 0.004$	$0.124 \pm 0.009$	$0.275 \pm 0.002$	
$k_s^c/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$3.3 \pm 0.2$	$2.8 \pm 0.1$	$1.94 \pm 0.01$	
$P_Y^c$	$0.16 \pm 0.01$	$0.32 \pm 0.02$	$0.705 \pm 0.005$	
$P_X(\text{CTAN})^d$	28	37	58	172
$P_X(\text{SDeS})^d$		5	13	32
$P_X(\text{SDS})^d$		16		100
$P_X(\text{NaPFO})^d$		34	53	77
$P_X(\text{NaPFN})^d$		260	323	481

<sup>a</sup> Butylthiourea. <sup>b</sup> Estimated by using the intercept and slope values obtained in accordance with eq 6 (see text). <sup>c</sup> Calculated by setting  $V = 0.390 \text{ dm}^3 \text{ mol}^{-1}$  (see text). <sup>d</sup> Estimated from data of refs 11 and 12 as described in the text.

$$k = \frac{k_{\text{obs}}}{[Y]} = \frac{k_w + k_s(\phi_s/\phi_w)P_M P_Y}{(1 + P_M \phi_s/\phi_w)(1 + P_Y \phi_s/\phi_w)\phi_w} \quad (5)$$

that an equivalent expression can be derived<sup>8</sup> by using a different kinetic treatment that considers the partition coefficients in terms of molar ratios of the species involved in each phase and of the ratios  $[\text{H}_2\text{O}]/[\text{AOT}]$  and  $[\text{oil}]/[\text{AOT}]$ .

The nonlinear least-squares analysis of the kinetic data has shown that, for all the three reactions examined, the rate constant  $k_w$  is negligibly small as compared to the other term in the numerator of eq 5 and that the quantity  $P_M \phi_s/\phi_w$  in the denominator is much larger than unity. As a consequence eq 5 reduces, after an appropriate rearrangement, to eq 6, which

$$\frac{1}{k} = \frac{V[\text{AOT}]}{k_s} + \left( \frac{0.018[\text{AOT}]}{k_s P_Y} \right) R \quad (6)$$

predicts a linear dependence of  $1/k$  on  $R$ . Figure 1 shows that straight lines are indeed obtained by plotting  $1/k$  as a function of  $R$ , providing support to the validity of the pseudophase model and the kinetic treatment employed in this work. The solid lines in this figure represent the least-squares fits (the correlation coefficients are higher than 0.998). It is worthwhile to note that no deviation from the linear trend is observed at the smaller  $R$  values examined, indicating the absence (or the negligible contribution) of specific effects upon the reaction rate caused by the state and the peculiar physicochemical properties of water<sup>7–9,15,17</sup> in the microemulsions (also termed reversed micelles) at low  $R$  values ( $\leq 10$ – $12$ ).

Table 2 assembles the values of  $k_s/V$  ( $=[\text{AOT}]/\text{intercept}$ , where  $[\text{AOT}] = 0.13 \text{ mol dm}^{-3}$ ) and  $k_s P_Y$  ( $= 0.018 [\text{AOT}]/\text{slope}$ ) obtained from the straight lines of Figure 1 as well as the values of the quantity  $VP_Y$  [ $= 0.018 \text{ intercept/slope} = (k_s P_Y)/(k_s/V)$ ]. Table 1 shows the good agreement between the experimental second-order rate constants  $k$  and those,  $k(\text{calc})$ , calculated by using these data and eq 6.

The present findings thus show that while weak partitioning of the thioureas occurs, the complex cation is strongly associated with the negatively charged AOT interface and that only the pathway involving the two reactants solubilized in the AOT interfacial region contributes significantly to the progress of the substitution reaction 1. Analogous results have been found before<sup>11,12</sup> for the same reactions in the presence of anionic hydrocarbon [SDS and sodium decyl sulfate (SDeS)] and perfluorocarbon [sodium perfluorooctanoate (NaPFO) and sodium perfluorononanoate (NaPFN)] micellar aggregates. Moreover, the kinetic data obtained previously<sup>13</sup> for reaction 1 using as entering ligands the anions  $\text{S}_2\text{O}_3^{2-}$  and  $\text{SCN}^-$  in the presence of SDS have allowed us to suggest that the palladium complex

under study is strongly bound to anionic SDS micelles by both electrostatic and hydrophobic interactions with a binding constant of  $2.2 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$ . The binding constant  $K_X$  of a species  $X$  partitioning between water and the micellar pseudophase is related<sup>3,14</sup> to the corresponding dimensionless partition coefficient ( $P_X$ ) by the expression  $P_X = K_X/V_m$ , where  $V_m$  can be set equal to the molar volume of the micellized surfactant. In the case of the palladium complex the estimated  $P_X$  is equal to  $8.8 \times 10^4$ , the value<sup>12,18</sup> of  $0.250 \text{ dm}^3 \text{ mol}^{-1}$  being used for  $V_m$  of the micellized SDS surfactant.

Inspection of Table 2 reveals that the quantity  $k_s/V$  decreases on passing from the nucleophile Tu to Me–Tu, and, then, to Et–Tu. We can calculate that the ratio  $k_s/V$  for Tu is 1.7 times larger than that for Et–Tu. Since the parameter  $V$  has to depend primarily on the physicochemical properties of the AOT interface and there is no reason for  $V$  to be (appreciably) influenced from the nature of the thioureas, for comparison purpose we can choose a given  $V$  value for all the cases examined and evaluate the second-order rate constant  $k_s$  from the  $k_s/V$  ratio. By setting  $V$  equal to the molar volume of the AOT surfactant (i.e.,  $0.390 \text{ dm}^3 \text{ mol}^{-1}$ ), the estimated rate constants  $k_s$  (Table 2) are found to be very close to the second-order rate constants  $k_{\text{aq}}$  (Table 1) for reactions in conventional aqueous solution, suggesting that the replacement of water coordinated to palladium by the thioureas proceeds by the same mechanism in the two different media. The same conclusion was also obtained previously by comparing the reactivities of the substitution process 1<sup>11,12</sup> and some metal–ligand complexation reactions<sup>3,19</sup> in bulk water with the corresponding reactivities in anionic micellar pseudophases. In this regard we recall that reduced rates have been found for reaction 1 taking place in anionic fluorinated micelles.<sup>12</sup>

As to the slight dependence of  $k_s$  on the type of nucleophile used (Table 2), it is possible to note that the order of reactivity in the AOT interface ( $\text{Tu} > \text{Me–Tu} > \text{Et–Tu}$ ) is different from that found<sup>11</sup> in homogeneous aqueous solution (cf. Table 1), where a balance between steric and inductive effects (acting in the opposite direction) of the alkyl group present in the thiourea molecule has been suggested to exist. Moreover, the observed order of reactivity is also opposite to that of the ligand hydrophobicity. Therefore it is reasonable to deduce that the steric hindrance brought about by the alkyl substituents hampers to some extent the attack of the nucleophile at the palladium, reducing thus the reaction rate in the interfacial AOT phase.

Adopting for  $V$  the same criterion as above, we can estimate the partition coefficient  $P_Y$  from the quantity  $VP_Y$  by using the  $V$  value of  $0.390 \text{ dm}^3 \text{ mol}^{-1}$ . Table 2 shows that the partition coefficient increases appreciably as the nucleophile becomes increasing hydrophobic, then following the order  $\text{Tu} < \text{Me–}$

Tu < Et–Tu. The relative  $P_Y$  values with respect to the unsubstituted thiourea are 1:2.0:4.4.

The partition coefficients  $P_Y$  of the thioureas estimated in this work can be compared (Table 2) with those ( $P_X$ ) derived from the corresponding binding constants ( $K_X$ ) obtained previously for monosubstituted thioureas in the presence of cationic<sup>11</sup> [cetyltrimethylammonium nitrate (CTAN)] and anionic<sup>11,12</sup> (SDeS, SDS, NaPFO, and NaPFN) micelles. The  $V_m$  values<sup>12</sup> used for the calculation of  $P_X (=K_X/V_m)$  are 0.207, 0.250, 0.214, and 0.235 dm<sup>3</sup> mol<sup>-1</sup> for SDeS,<sup>20</sup> SDS,<sup>18</sup> NaPFO,<sup>21</sup> and NaPFN,<sup>22</sup> respectively. For CTAN the value<sup>23</sup> of  $V_m = 0.360$  dm<sup>3</sup> mol<sup>-1</sup> relative to the bromide derivative has been used. The result of this comparison is that partitioning of a given nucleophilic substrate between the water pools and the AOT interface of the microemulsion is remarkably smaller than that between water and both cationic and anionic micelles.

The observed dependence of the partition coefficient  $P_Y$  on the hydrophobic character of the nucleophile can also be evidenced by estimating<sup>24,25</sup> the contribution ( $\Delta\mu_c^\circ$ ) of a carbon atom of the alkyl group (that is, a methylene or methyl moiety) to the standard Gibbs free energy of transfer  $\Delta\mu^\circ (= -RT \ln P_Y)$  per mole of substrate from the water pools to the AOT interface. The incremental Gibbs energy of transfer  $\Delta\mu_c^\circ$  represents the slope of the linear plot of  $\Delta\mu^\circ$  as a function of the number of carbon atoms of the alkyl group present in the thiourea molecule. The estimated  $\Delta\mu_c^\circ$  value ( $= -1.83 \pm 0.07$  kJ mol<sup>-1</sup>) is more negative than the  $\Delta\mu_c^\circ$  values obtained previously<sup>11,12</sup> for the transfer of monosubstituted thioureas from water to both cationic and anionic micelles ( $\Delta\mu_c^\circ = -1.1, -1.5, -1.5, -0.6$ , and  $-0.51$  kJ mol<sup>-1</sup> for CTAN, SDeS, SDS, NaPFO, and NaPFN, respectively). This result together with that found above leads to the concluding suggestion that, even though the solubilization of the thioureas in the AOT interfacial region of the microemulsion is smaller as compared to that in micelles, the hydrophobic interactions involved in the solubilization process are more significant in the AOT interface than in cationic and anionic micelles.

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