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# Transfer of the Nitroso Group in Water/AOT/Isooctane Microemulsions: Intrinsic and Apparent Reactivity

Luis García-Río, J. Ramón Leis,\* and M. Elena Peña

Departamento de Química Física, Facultad de Química, Universidad de Santiago, Santiago de Compostela, Spain

Emilia Iglesias\*

Departamento de Química Fundamental e Industrial, Facultad de Ciencias, Universidad de La Coruña, La Coruña, Spain

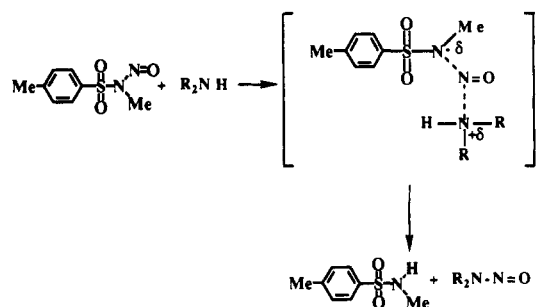
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The kinetics of the transfer of the nitroso group from *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide to each of seven secondary amines (piperazine, *N*-methylbenzylamine, piperidine, dimethylamine, morpholine, pyrrolidine, and diisopropylamine) was studied using a wide variety of water/AOT/isooctane microemulsions as reaction media. The diverse kinetic behavior of the various amines can be explained quantitatively on the basis of a single model taking into account the distribution of the amine among the aqueous and isooctane phases and their mutual interface; the reaction itself always takes place at the interface. The relative reactivities of the amines are discussed in comparison with the order observed in water.

## Introduction

Chemical reactivity in microemulsions is an attractive object of study because these media are macroscopically homogeneous and isotropic but are heterogeneous on the molecular scale. Water in oil (w/o) microemulsions contain aqueous microdroplets wrapped in a film of surfactant and dispersed in a low-polarity bulk solvent.<sup>1,2</sup> The reagents present in the medium may be separated in different microscopic phases or may share the same phase, and the kinetics of their reactions will reflect their various distributions. Apart from these purely chemical considerations, microemulsions are of interest as reaction media because of similarities with certain biological systems. They share with biological membrane systems the separation between polar and apolar regions and their surfactant-trapped aqueous microdroplets can be considered as models of water trapped in enzymes or other biological structures.<sup>3-5</sup> Accordingly, great effort has in recent years been devoted to the study of aqueous microdroplets, generally in water/sodium bis(2-ethylhexyl)sulfosuccinate (AOT)/alkane microemulsions, which can contain large quantities of water and in which droplet size is controlled by the water/AOT ratio.<sup>1,2,6</sup> This research suggests that the physical characteristics of microdroplet water differ from those of bulk water, especially as regards mobility, polarity, and properties affected by its high ionic strength and by the electrical influence of the charged surfactant heads.<sup>6-12</sup> There have also been interesting reports on the kinetics of chemical reactions in w/o microemulsions,<sup>13-19</sup> but few of these studies have been quantitative (in contrast with kinetics in normal micelles). Prediction and/or interpretation of the kinetic influence of these media is relatively easy when both reagents congregate in the aqueous microdroplets which act as variable-size nanoreactors concentrating the reagents.<sup>20-22</sup> Less attention has been paid to reactions in which the reagents are distributed in the aqueous and apolar phases and at their interface.<sup>23</sup> In this article we report the kinetics of nitrosation of six secondary amines by *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (MNTS) in water/AOT/isooctane microemulsions (see Scheme I). The amines (piperazine, *N*-methylbenzylamine, piperidine, dimethylamine, morpholine, and pyrrolidine) were chosen to allow comparisons between amines resident in different phases and between amines with different basicity in water (to determine whether, as in water, it is their basicity that controls

## SCHEME I



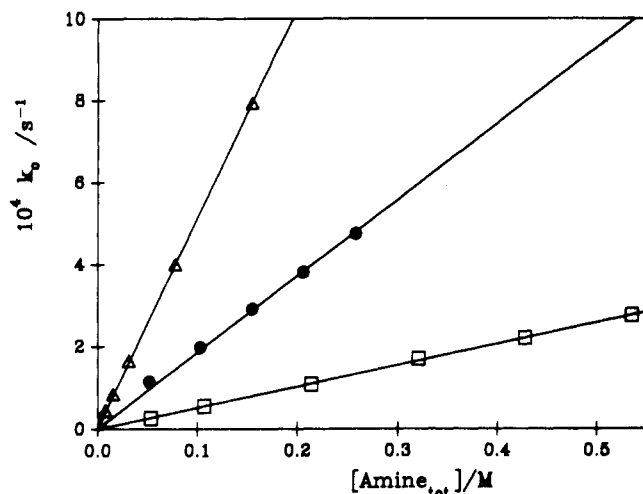
the reactivity of the amines). Our results have been quantitatively interpreted and shed light on the different aspects that control the apparent reactivity in microheterogeneous systems.

## Experimental Section

AOT (Aldrich) was dried for 2 days in a vacuum desiccator and used without further purification. *N*-Methylbenzylamine (Aldrich) was purified by distillation under an argon atmosphere. All other reagents were supplied by Merck and were used without further purification.

Kinetic measurements were carried out at 25 or 35 °C in Kontron-Uvikon 930 or Spectronic 3000 Diode Array spectrophotometers equipped with thermostated cell carriers. For piperazine, piperidine, pyrrolidine, and dimethylamine, the disappearance of the absorbance at 260 nm due to MNTS consumption was followed and the initial MNTS concentration was  $1.91 \times 10^{-4}$  M. In the case of *N*-methylbenzylamine, its high molar absorptivity precluded studying the reaction at 260 nm; it was therefore necessary to follow the reaction at 392 nm, using an initial MNTS concentration of  $2 \times 10^{-3}$  M. A similar procedure was followed in the case of morpholine. The MNTS concentration was always very much less than the concentration of amine. The kinetic data always fitted the first-order integrated equation satisfactorily ( $r > 0.999$ ); in what follows,  $k_o$  denotes the first order pseudoconstant.

To determine partition coefficients for the distribution of the amines between pure isooctane and pure water, mixtures of amines with measured quantities of the solvents were left to equilibrate



**Figure 1.** Influence of the total amine concentration upon  $k_o$  at 25 °C. ( $\Delta$ ) Piperazine,  $[AOT] = 0.47$  M,  $w = 15.8$ ; ( $\bullet$ ) *N*-methylbenzylamine,  $[AOT] = 0.43$  M,  $w = 13$ ; ( $\square$ ) Morpholine,  $[AOT] = 0.71$  M,  $w = 13$ .

by continuous stirring for 1 week at 25 °C. The amine content of the aqueous phase was determined by titration against hydrochloric acid, with a mixture of methyl red and bromocresol green as indicator.

Densities were measured with a pycnometer.

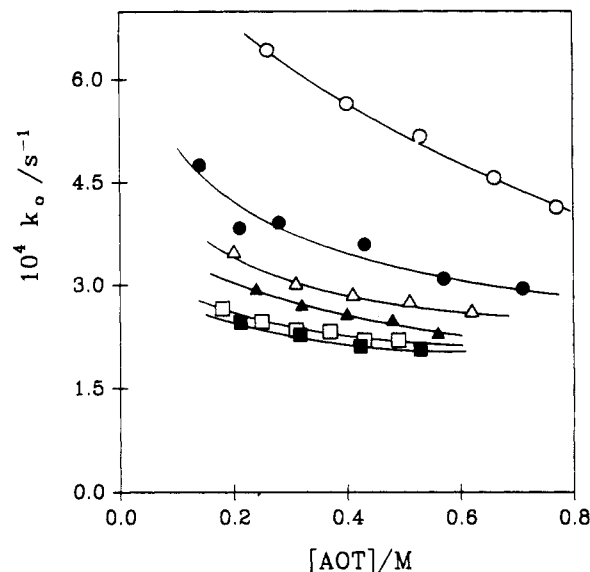
## Results and Discussion

MNTS reacts with secondary amines by transnitrosation to give carcinogenic *N*-nitrosamines.<sup>24</sup> The rate equations obtained for the reactions in microemulsions were in all cases similar to those in water, with first-order terms in MNTS and total amine concentration (some examples are shown in Figure 1). We worked under conditions in which ionization of the amines in water is negligible. Competing hydrolysis of MNTS by the small amount of hydroxyl ions liberated by this ionization is insignificant, because solutions of MNTS with as much as  $2 \times 10^{-2}$  M  $OH^-$  (referred to the total volume of solution) are stable for long periods of time (several days). UV-vis spectra at the end of the reaction indicated quantitative nitrosamine formation in every case.

**Reaction with Piperazine.** A series of experiments were performed at 25 °C at fixed amine concentration and variable AOT concentration (typically between 0.15 and 0.7 M) with the water/AOT mole ratio,  $w$ , fixed at values ranging from 7 to 35. This wide range of  $w$  values was used so as to be able to compare reactivity and partition results obtained under conditions differing significantly as regards the physical state of the water in the medium. At  $w = 7$ , most of the water is probably solvating surfactant heads or sodium ions and hence has a highly rigid, microviscous "icelike" structure, whereas at  $w = 35$  most of the water present has the properties of bulk water.

At constant  $w$ , the observed reaction rate fell slightly as the concentration of AOT increased, while for constant AOT concentration the reaction rate fell with increasing  $w$  (although the increase from  $w = 7$  to  $w = 35$  reduced the rate no more than 3-fold); see Figure 2. To interpret these results, it should be borne in mind that MNTS is very poorly soluble in water and that piperazine is virtually insoluble in isooctane (the partition coefficient  $K_{oil,water}$ , defined as the ratio between the mole fractions of solute in water and isooctane, is over 50; see Table I). In microemulsions, piperazine and MNTS can therefore react only at the interface, with the surfactant providing a new region where contact between the reagents becomes possible. AOT can be considered as acting as a phase transfer catalyst.

A quantitative model for the above situation may be constructed by extending the pseudophase model to include three pseudophases (water, isooctane, and AOT), each of which is considered as being uniformly distributed in the total volume of the microemulsion.



**Figure 2.** Influence of the concentration of AOT upon  $k_o$  for the nitrosation of piperazine by MNTS at constant  $w$ .  $[Piperazine_{tot}] = 5 \times 10^{-2}$  M; ( $\circ$ )  $w = 7$ ; ( $\bullet$ )  $w = 13$ ; ( $\Delta$ )  $w = 18$ ; ( $\blacktriangle$ )  $w = 23$ ; ( $\square$ )  $w = 30$ ; ( $\blacksquare$ )  $w = 35$ . Lines are drawn to help the eye.  $T = 25$  °C.

**TABLE I: Values of  $K_{oil,water}$  for the Partition of Secondary Amines between Water and Isooctane at 25 °C**

amine	$K_{oil,water}$	amine	$K_{oil,water}$
piperazine	>50	dimethylamine	1.3
<i>N</i> -methylbenzylamine	0.04	pyrrolidine	6.4
piperidine	0.3 (0.1 at ionic strength 6 M)	morpholine	1.3

In view of the solubility characteristics of MNTS and piperazine, the distribution of the reagents among these pseudophases can be described by the partition coefficients

$$K_{MNTS} = \frac{[MNTS_i][isooctane]}{[MNTS_o][AOT]} \quad (1)$$

$$K_i = \frac{[amine_i][H_2O]}{[amine_w][AOT]} \quad (2)$$

where the subscripts  $w$ ,  $o$ , and  $i$  indicate respectively the aqueous, oil, and AOT (interface) phases, and the concentrations in square brackets refer to the total volume of microemulsion (as is usual practice in normal micelles<sup>25</sup>). Partition coefficients have been expressed in terms of mole ratios in each phase, a choice that makes the kinetic treatment much easier. Problems and approximations involved in these definitions have been discussed in the literature.<sup>26</sup> Because the reaction takes place at the interface, the pseudo-rate constant  $k_o$  is given by

$$k_o = \frac{k'_i K_{MNTS} [AOT]}{K_{MNTS} [AOT] + [isooctane]} \quad (3)$$

where  $k'_i$ , the first-order pseudo-constant for the reaction in the AOT phase, can be expressed in terms of a bimolecular interfacial rate constant  $k_i$  and the mole ratio between the piperazine at the interface and the AOT (this definition avoids having to define explicitly the mole reaction volume of the interface):

$$k'_i = k_i [amine_i] / [AOT] \quad (4)$$

Equations 1–4, together with the mass balance for the amine, yield

$$k_o = \frac{k_i K_{MNTS} K_i [amine_{tot}] [AOT]}{(K_{MNTS} [AOT] + [isooctane]) (K_i [AOT] + [H_2O])} \quad (5)$$

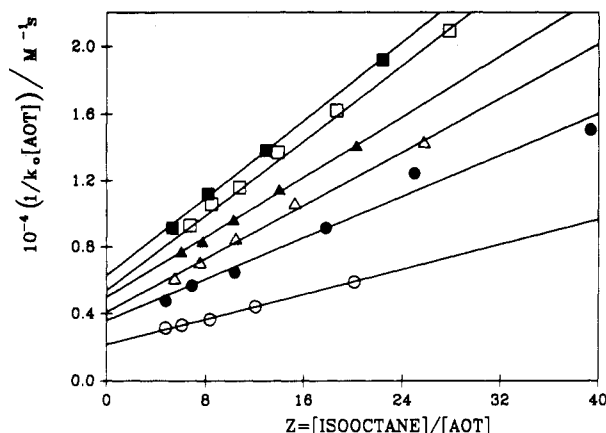


Figure 3. Linearization of data from Figure 2 as predicted from eq 6 (see text).

TABLE II: Slopes and Intercepts at the Origin Obtained upon Fitting  $1/k_o[AOT]$  vs  $z$  (Figure 3) to the Experimental Kinetic Data for the Reactions of Piperazine with MNTS in Water/AOT/Isooctane Microemulsions at 25 °C

$w$	$10^{-3}$ intercept/ $M^{-1} s$	$10^{-2}$ slope/ $M^{-1} s$	$K_{MNTS} =$ intercept/slope
7	$2.17 \pm 0.06$	$1.87 \pm 0.05$	11.6
13	$3.6 \pm 0.5$	$3.1 \pm 0.2$	11.6
18	$4.1 \pm 0.2$	$4.0 \pm 0.1$	10.3
23	$5.0 \pm 0.1$	$4.5 \pm 0.1$	11.1
30	$5.4 \pm 0.5$	$5.6 \pm 0.3$	9.6
35	$6.3 \pm 0.2$	$5.8 \pm 0.1$	10.9

To simplify these expressions, in what follows we denote the isooctane/AOT mole ratio by  $z$ , in analogy with the more familiar parameter  $w$ . Then equation 5 reduces to

$$k_o = \frac{k_i K_{MNTS} K_1 [\text{amine}_{\text{tot}}]}{(K_{MNTS} + z)(K_1 + w)[AOT]} \quad (6)$$

Figure 3 shows that, in agreement with this equation,  $1/(k_o[AOT])$  depends linearly on  $z$  for each fixed value of  $w$  and that both the slope and the intercept at the origin increase with  $w$ , and Table II shows that there is good agreement among the values of  $K_{MNTS}$  calculated, for the various values of  $w$ , from the ratio between the intercept at the origin and the slope. The average value for  $K_{MNTS}$  is 11, in good agreement with the value of about 10 estimated for the MNTS-AOT association constant by analysis of changes in the UV spectrum of MNTS at 265–275 nm. It should be borne in mind that precise spectroscopic estimation of this constant is ruled out by the impossibility of having all the MNTS in the interface. Our spectroscopic estimation of  $K_{MNTS}$  was therefore based on an analysis of the spectroscopic data using a fitting procedure with the absorbance of MNTS when fully bound to the interface as an optimizable parameter.

Conventional analysis of slopes and intercepts of the results in Figure 3 (eq 6) afforded the values of  $K_1$  and  $k_i$  listed in Table III. All the experimental data are satisfactorily accounted for by eq 6 with a mean deviation of less than 5%.

Additional experiments were carried out at 35 °C. This allowed kinetic measurements to be taken in a wider range of microemulsion composition (up to  $w = 50$ ). At this temperature the systems show low conductivity at low  $w$ , but the onset of the percolation phenomenon can be reached upon increasing  $w$ . Our kinetic model (eq 6) was found to satisfactorily fit the experimental data, which displayed kinetic features similar to those found at 25 °C. A value of 9.8 for  $K_1$  was obtained, showing little change in MNTS partition with this moderate increase in temperature. Values for other kinetic and thermodynamic parameters are found in Table III.

**Reaction with *N*-Methylbenzylamine and Piperidine.** The kinetics of the nitrosation of *N*-methylbenzylamine by MNTS,

studied at 25 °C and constant amine concentration, exhibited the opposite trends to those observed for piperazine: the reaction rate increased with increasing AOT concentration and with increasing  $w$  (Figure 4). Since *N*-methylbenzylamine, unlike piperazine, is poorly soluble in water ( $K_{\text{oi,water}} = 0.04$ ; Table I), the amount of amine dissolved in the aqueous phase should be negligible, and the reaction will in principle be limited to two of the three pseudophases present, i.e. the isooctane phase and the interface. However, the observed rate constants for reaction of MNTS with *N*-methylbenzylamine (and other amines) in pure isooctane is several orders of magnitude slower than the rate constants observed in the microemulsions, showing that, as in the case of piperazine, in w/o microemulsions the reaction effectively takes place only in the AOT pseudophase of the interface.  $K_2$ , the partition constant of amine between AOT and isooctane, is given by

$$K_2 = \frac{[\text{amine}_i][\text{isooctane}]}{[\text{amine}_o][AOT]} \quad (7)$$

Similar reasoning to that used above for piperazine leads to

$$k_o = \frac{k_i K_{MNTS} K_2 [\text{amine}_{\text{tot}}]}{[AOT](K_{MNTS} + z)(K_2 + z)} \quad (8)$$

Because neither reagent is present in the aqueous phase, eq 8, unlike eq 6, does not contain  $w$ . Note that for fixed AOT concentration, increasing  $w$  (i.e., increasing the size of the water droplets) reduces the concentration of isooctane and therefore  $z$ . This inverse dependence of  $z$  on  $w$  gives rise to the increase in the reaction rate with  $w$  observed in Figure 4. Equation 8 likewise correctly predicts the observed increase in reaction rate with AOT concentration (decrease in  $z$ ) for fixed  $w$ . A modified form of eq 8

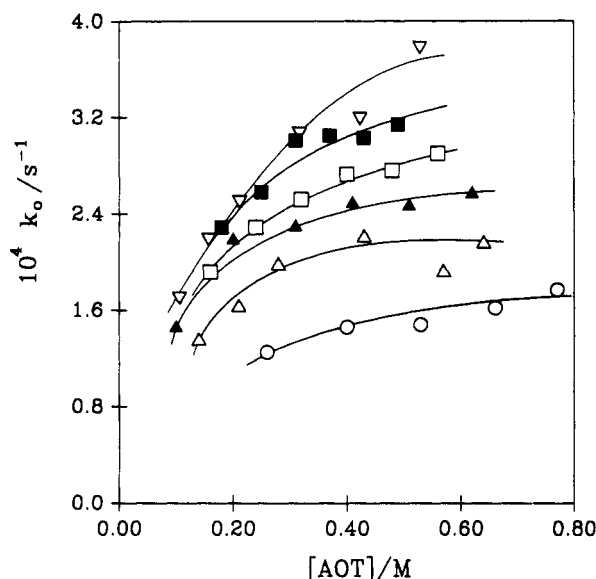
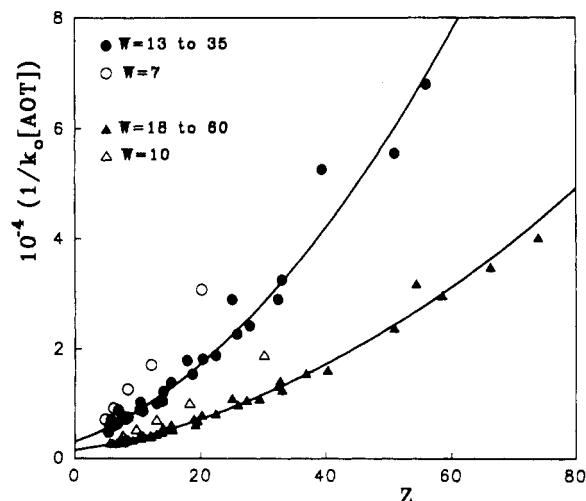
$$\frac{1}{k_o[AOT]} = \frac{(K_{MNTS} + z)(K_2 + z)}{k_i K_{MNTS} K_2 [\text{amine}_{\text{tot}}]} \quad (9)$$

predicts that  $1/(k_o[AOT])$  depends quadratically upon  $z$ , as experimentally found (Figure 5). Assuming the value of  $K_{MNTS}$  is the same as that obtained in the experiments with piperazine, the values of  $K_2$  and  $k_i$  were estimated (Table III) by fitting eq 9 to 32 of the 37 experimental data points at 25 °C by means of an optimization procedure based on Marquardt's method<sup>27</sup> (Figure 5). The five data points not used for the optimization procedure all correspond to  $w = 7$ . The reaction is slower than predicted in the smallest aqueous droplets, perhaps because the hydration of the interface, and hence its effective dielectric constant, are reduced when so little water is present. This kind of reaction is known to be slowed by media with low dielectric constants.<sup>24</sup> Indeed, there is experimental evidence that the dielectric constant of the interface of small droplets ( $w < 10$ ) gradually increases with  $w$ .<sup>28</sup> The fact that eq 9 fits the experimental data for  $w > 10$  very well is in keeping with the notion that water added above this value is not required for hydration of surfactant heads or counterions, but makes up a core with properties similar to those of bulk water.<sup>29,30</sup> Insufficient hydration of the interface at low water concentrations may also affect the thermodynamic constants for partition of the reagents between isooctane and AOT. Experiments carried out at 35 °C (Figure 5) also show close agreement between the experimental data and the predictions of our model. Deviations are again observed at  $w < 10$ , but the validity of our model now extends up to  $w = 60$  and to regions with electrical percolation. Table III shows the results of the fitting procedure at this temperature, using for  $K_{MNTS}$  the value of 9.8 previously found for this temperature.

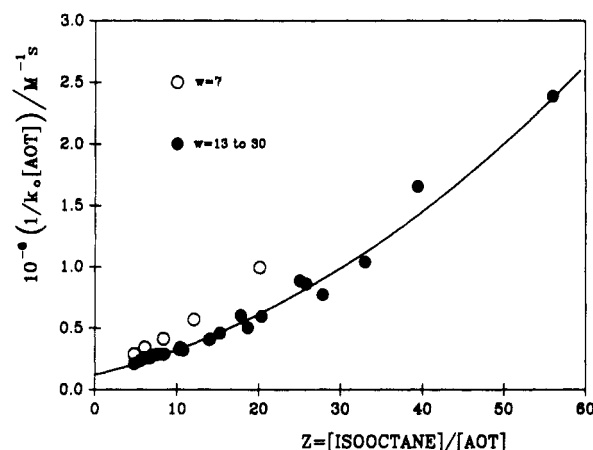
Similar behavior was observed when piperidine was used as substrate instead of *N*-methylbenzylamine, in spite of piperidine being much more soluble in water ( $K_{\text{oi,water}} = 0.3$ ; see Table I). The reaction rate (at 25 °C) again increased with AOT

**TABLE III: Kinetic Parameters and Partition Coefficients Estimated by Fitting Eqs 6, 9, or 10 to the Experimental Kinetic Data for the Reaction of Secondary Amines with MNTS in Water/AOT/Isooctane Microemulsions ( $k_i$ ,  $K_1$ ,  $K_2$ ) or Water ( $k_w$ )**

amine	$k_i/s^{-1}$	$K_1$	$K_2$	$k_2^1/M^{-1}s^{-1}$	$k_w/M^{-1}s^{-1}$
piperazine <sup>a</sup>	$1.45 \times 10^{-2}$	9.5		$5.33 \times 10^{-3}$	$2.98 \times 10^{-2c}$
piperazine <sup>b</sup>	$3.18 \times 10^{-2}$	13.1			
<i>N</i> -methylbenzylamine <sup>a</sup>	$3.1 \times 10^{-3}$		25.6	$1.0 \times 10^{-3}$	$4.1 \times 10^{-2c}$
<i>N</i> -methylbenzylamine <sup>b</sup>	$6.9 \times 10^{-3}$		30		
piperidine	$8.1 \times 10^{-3}$		25.7	$3.0 \times 10^{-3}$	0.160 <sup>c</sup>
dimethylamine	$4.4 \times 10^{-2}$	83.3	83.3	$1.6 \times 10^{-2}$	0.384 <sup>c</sup>
morpholine <sup>a</sup>	$6.5 \times 10^{-4}$	46.9	ca. 600	$2.4 \times 10^{-4}$	$4.96 \times 10^{-3c}$
morpholine <sup>b</sup>	$1.76 \times 10^{-3}$	52	200		
pyrrolidine	0.12	8.33	ca. 125	$4.22 \times 10^{-2}$	0.83 <sup>c</sup>
diisopropylamine	too slow to measure				$1.12 \times 10^{-2c}$

<sup>a</sup> At 25 °C. <sup>b</sup> At 35 °C. <sup>c</sup> Taken from ref 24.**Figure 4.** Influence of the concentration of AOT upon the pseudo-first-order rate constant for nitrosation of *N*-methylbenzylamine by MNTS at constant  $w$ . [*N*-Methylbenzylamine]<sub>tot</sub> = 0.103 M. (○)  $w = 7$ ; (Δ)  $w = 13$ ; (▲)  $w = 18$ ; (□)  $w = 23$ ; (■)  $w = 30$ ; (▽)  $w = 35$ . Lines are drawn to help the eye.  $T = 25$  °C.**Figure 5.** Plot of  $1/(k_o[AOT])$  vs  $z$  for the nitrosation of *N*-methylbenzylamine by MNTS. The solid line is the theoretical line predicted by eq 9 (parameters in Table III). [*N*-Methylbenzylamine]<sub>tot</sub> = 0.103 M. Circles and triangles refer to reactions at 25 and 35 °C, respectively.

concentration (for fixed  $w$ ) and with  $w$  (for fixed  $[AOT]$ ), and  $1/(k_o[AOT])$  again depended quadratically on  $z$  (Figure 6; see Table III for the optimized parameters of eq 9). The apparent paradox disappears when the compositions of the microemulsions are taken into account, since together with  $K_{oil}^{water}$  and  $K_2$  they imply that no more than about 20% of the piperidine can be

**Figure 6.** Plot of  $1/(k_o[AOT])$  vs  $z$  for the nitrosation of piperidine by MNTS. The solid line is the theoretical line predicted by eq 9 (parameters in Table III). [Piperidine]<sub>tot</sub> = 0.101 M.  $T = 25$  °C.

present in the water phase. Alternatively, or additionally, the differences between the physicochemical properties of bulk water and water trapped in microdroplets may mean that the values of  $K_{oil}^{water}$  measured in a macroscopic two-phase system are not good approximations for the corresponding partition constants in the microemulsion.<sup>23</sup> In this case our data suggest that piperidine has less affinity for microdroplet water than for bulk water. Table I shows that  $K_{oil}^{water}$  decreases upon increasing the ionic strength in the water phase. The ionic strength corresponding to the aqueous core of the microemulsions used can be on the order of 3–5 M, consistent with the low affinity of piperidine for the microemulsion aqueous phase.

**Reaction with Dimethylamine, Morpholine, and Pyrrolidine.** The behavior of dimethylamine was at first sight surprising. In series of experiments in which, at 25 °C,  $[AOT]$  was varied for fixed values of  $w$  between 7 and 35, the observed rate constant hardly changed (Table IV). Because dimethylamine does not appear to partition strongly to either oil or water (see Table I), it is probably present in all three pseudophases in the microemulsion, a more complex situation than any of those considered above. However, the effective reaction region is still constituted by the interface alone, because reaction in isooctane is much slower than the observed rates. The corresponding expression for  $k_o$  is

$$k_o = \frac{k_i K_{MNTS} [\text{amine}]_{tot}}{[AOT] (K_{MNTS} + z) \left( 1 + \frac{w}{K_1} + \frac{z}{K_2} \right)} \quad (10)$$

which contains both  $w$  and  $z$ . Equation 10, with  $K_{MNTS}$  set equal to 11 as before, satisfactorily fits the experimental data (mean deviation 9%, or 7% if the data for  $w = 7$  were excluded) using the parameters listed in Table III. Table IV shows that the chief discrepancies between the experimental values of  $k_o$  and those predicted by this equation again occur when very little water is

**TABLE IV: Experimental and Theoretical Values of  $k_0$  ( $s^{-1}$ ) for Nitrosation of Dimethylamine ( $4.17 \times 10^{-2}$  M) and Morpholine (0.107 M) at 25 °C**

[AOT]/M	z	w	dimethylamine		morpholine	
			$10^3 k_0^a$	$10^3 k_0^b$	$10^3 k_0^a$	$10^3 k_0^b$
0.26	20	7	1.28 <sup>c</sup>	1.87 <sup>d</sup>	7.91	7.97
0.40	12	7	1.34 <sup>c</sup>	1.77 <sup>d</sup>	6.34	7.07
0.53	8.3	7	1.30 <sup>c</sup>	1.65 <sup>d</sup>	5.91	6.40
0.66	6.1	7	1.38 <sup>c</sup>	1.46 <sup>d</sup>	6.05	5.84
0.77	4.8	7	1.32 <sup>c</sup>	1.45 <sup>d</sup>	5.18	5.43
0.14	39	13	1.53	1.72	7.81	8.06
0.21	25	13	1.67	1.79	8.40	7.65
0.28	18	13	1.75	1.79	7.96	7.24
0.43	10	13	1.67	1.67	6.91	6.41
0.57	6.9	13	1.51	1.55	6.39	5.81
0.71	4.8	13	1.52	1.44	4.66	5.30
0.10	56	18	1.48	1.56	7.52	7.70
0.20	26	18	1.78	1.75	7.16	7.26
0.31	15	18	1.65	1.73	6.64	6.65
0.41	10.5	18	1.62	1.66	6.23	6.19
0.51	7.5	18	1.48	1.59	5.91	5.77
0.62	5.5	18	1.70	1.50	4.60	5.35
0.16	33	23	1.80	1.68	6.96	7.02
0.24	20	23	1.73	1.72	6.84	6.66
0.32	14	23	1.72	1.70	6.42	6.29
0.40	10	23	1.68	1.66	6.25	5.95
0.48	7.8	23	1.67	1.59	5.74	5.64
0.56	6.0	23	1.74	1.52	5.44	5.33
0.18	28	30	1.83	1.66	6.23	6.47
0.25	19	30	1.67	1.67	6.14	6.15
0.31	14	30	1.50	1.66	6.37	5.93
0.37	11	30	1.55	1.64	5.85	5.72
0.43	8.5	30	1.41	1.60	5.47	5.51
0.49	6.7	30	1.49	1.57	5.27	5.32
0.11	51	35	1.62	1.48	6.35	6.35
0.16	32	35	—	—	6.06	6.23
0.21	22	35	1.75	1.64	5.84	6.04
0.32	13	35	1.54	1.64	5.19	5.69
0.41	8.3	35	1.44	1.58	5.29	5.34
0.53	5.3	35	1.51	1.53	—	—

<sup>a</sup> Experimental data. <sup>b</sup> Calculated data. <sup>c</sup> Excluded from the fitting procedure (see text). <sup>d</sup> Calculated from eq 10 using parameters in Table III.

present ( $w = 7$ ). Further support for the model comes from the value of the ratio  $K_2/K_1$ , which is partition of dimethylamine between oil and water. The optimized value equals 1, in good agreement with the measured value for partition between the same macrophases (Table I).

Equation 10 also satisfactorily explained the behavior observed at 25 °C for reaction of MNTS with morpholine (data in Table IV) or pyrrolidine (results not shown). These amines, like DMA, are present in both water and isooctane phases of the microemulsions, although partition to water is much favored (see Table I). The experimental trends in  $k_0$  are intermediate between those observed for piperazine and for dimethylamine. The amount of morpholine in isooctane must be quite low, because the data could be also fitted—although with somewhat greater deviations—to the model used in the case of piperazine (eq 6). However, results obtained at 35 °C can only be fitted if partition of the amine among all three phases is considered. The main deviation from eq 10 in the case of pyrrolidine concerned again data for  $w = 7$ , whereas all the morpholine data could be fitted to eq 10 with a mean deviation of 6%. Table III lists the optimized parameters of eq 10.

**Comparison of the Results.** In all the cases considered above, the results can be interpreted by assuming that the reaction occurs at the interface between the water droplet and the isooctane and that the dependence of the observed rate constants on reaction conditions is governed largely by the relative affinities of the amine for the different phases present in the medium. The hydrophobicity of the amine determines its distribution between the three phases and whether the rate constant increases (Figure

4), decreases (Figure 2) or remains essentially constant (Table IV) as droplet size increases. These results are particularly satisfying because very different kinetic behaviors all find satisfactory quantitative explanation in terms of a single theoretical model for all droplet sizes except the very smallest. This agreement with the model might look surprising if we consider that no corrections have been introduced to take into account any increase in the volume of the interface due to the incorporation of amine,<sup>31</sup> but under the conditions used, this influence must be almost negligible.<sup>32</sup> Our results also seem to support our definition of partition coefficients in terms of mole ratios and not of mole fractions (such a difference will only be significant in those experiments in which the concentration of amine incorporated to AOT is not negligible with respect to AOT concentration). Recent results from our laboratory<sup>33</sup> confirm this choice.

The electrical conductivity of the microemulsions for these nitroso transfer reactions ranged from low, i.e., small water droplets dispersed in an oily medium, to high, probably due to percolation effect, i.e., droplet clusters that are internally connected by water channels.<sup>34</sup> The fact that such a great difference in charge transport properties does not appear to influence chemical reactivity in microemulsions strengthens the confidence that can be placed in the pseudophase model (which treats the water, oil, and interfacial regions as separate phases and ignores the structural characteristics of the droplets). No doubt this approximation is valid for chemically controlled reactions whose rate is slow compared to the rate of exchange of matter between droplets, which takes place on a much shorter (millisecond) time scale.<sup>35</sup>

In the present study, the pseudophase model allows the thermodynamic problem of partition among the phases to be separated from the kinetic problem and therefore estimate the reactivity of the different amines in the interfacial region,  $k_i$ . Though not a conventional second order rate constant (its unit is  $s^{-1}$ ), the values of  $k_i$  in Table III show the relative reactivities of the various amines at the interface and can be compared with the corresponding reactivity in bulk water. Table III lists values for  $k_w$ , the second-order rate constant determined in water containing a very small proportion of organic cosolvent (usually 3.3% dioxane), needed to dissolve MNTS in water. The order of reactivity in water<sup>24b</sup> is: pyrrolidine > dimethylamine > piperidine > *N*-methylbenzylamine > piperazine > morpholine. The respective rate constant ratios are 167:77:32:8:6:1. This order parallels the basicity of the amines, except for dimethylamine which is less sterically hindered and therefore more reactive than would be expected on the basis of its  $pK_a$ .<sup>24</sup> In the AOT interface, the corresponding rate constants ratios are 185:68:13:5:49:1. Except for piperazine now being considerably more reactive than piperidine or *N*-methylbenzylamine, the order is the same as in water. In fact, plots of  $\log k$  vs  $pK_a$  give similar slopes, ca. 0.6, both in water and AOT—excluding the point for piperazine. The increased relative reactivity of piperazine may be due to its two equivalent N atoms, endowing it with a statistical advantage. This advantage may be enhanced when the mobility of the substrate molecule is reduced by entrapment in the interface. The notion that the reaction is very sensitive to steric hindrance is confirmed by the fact that diisopropylamine ( $pK_a$  11.2), which is more basic than dimethylamine, reacts in water some 30 times slower than dimethylamine (see Table III). The steric problem seems harder to overcome for reaction in the interface, probably due to difficulties arising from the restricted mobility of the substrates. We have been unable to detect any hint of reaction between MNTS and diisopropylamine in AOT microemulsions, even when monitoring the mixture for several hours.

Finally, absolute comparison of reactivities in water and AOT would require knowledge of the molar reaction volume at the interface. An estimation of this volume can be made by combining the density of AOT in the microemulsion (1.2 g/mL<sup>36</sup>) and its

molecular weight. This yields a value of  $0.37 \text{ M}^{-1}$  for the molar volume of AOT in the microemulsion, which can be taken as the molar reaction volume,  $\bar{V}$ . A conventional second order rate constant (with conventional units,  $\text{M}^{-1} \text{ s}^{-1}$ ) is given by

$$k_2^i = k_i \bar{V} \quad (11)$$

Values of  $k_2^i$  are also summarized in Table III. Comparison of these values with those corresponding to reaction in bulk water shows that the nitroso transfer reactions are 20–50 times slower at the interface of the microemulsion, which can be attributed to the lower polarity of the interfacial region. As shown in Scheme I the transition state for our reaction requires a certain degree of charge separation, and reduction of the polarity will cause a decrease in reaction rate.<sup>24</sup> This explanation is consistent with the lower reactivities observed for  $w = 7$ –10, where incomplete hydration of the interface may lower the polarity of the interface.

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