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S_N2 Displacement by Bromide Ions in Dichloromethane – The Role of Reverse Micelles

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Reverse micellar systems are of interest as reaction media because they are powerful models for biological compartmentalization, enzymatic catalysis and separation of biomolecules. Solutions of ionic surfactants in apolar solvents may contain reverse micelles, but they may also contain ion pairs, or small clusters, with waters of hydration. We studied the bimolecular reaction in CH_2Cl_2 solutions of cationic tetraalkylammonium bromide salts (onium salts), such as cetyltrimethylammonium bromide (CTABr), cetyltripropylammonium bromide (CTPABr) and tetra-*n*-butylammonium bromide (TBABr). Methylnaphthalene-2-sulfonate (β-MeONs), its 6-sulfonate derivative (β-MeONsS$^-$) as the 2,6-lutidinium salt and methyl-5-*N*,*N*,*N*,trimethylammonium naphthalene-1-sulfonate (α-MeONsNT$^+$) as the trifluoromethanesulfonate salt react with Br^- in CH_2Cl_2. First-order rate constants, k_{obs}, increase linearly and similarly for the three substrates with increasing concentrations of the onium salts. Reactions are faster with TBABr than they are with CTPABr and CTABr, and the reactivity of the three substrates is in the order: α-MeONsNT$^+$ >> β-MeONsS$^-$ > β-MeONs. The reactions are inhibited by the addition of H_2O, but CTABr tolerates H_2O in large excess. At $[H_2O]/[CTABr] = w_0 \approx 6$, "water-pool" reverse micelles form, and k_{obs} for all three substrates is then independent of w_0.

Introduction

Reverse micelles are of interest as reaction media because they are models for biological compartmentalization and enzymatic catalysis.[1–2] Reverse micelles are macroscopically homogeneous, but heterogeneous on the nanoscale. Each micelle is a nanodroplet-sized water pool encased in a surfactant film dispersed in a low-polarity solvent.[1–3] Two clearly differentiated aqueous and organic regions compartmentalize water- and oil-soluble solutes and solutes having both hydrophobic and hydrophilic groups may be located in the surfactant film close to the surfactant's headgroups. Reverse micelles formed by the surfactant sodium bis(2-ethylhexyl)sulfosuccinate (AOT) in apolar solvents have been especially studied,[4–8] but cationic surfactants can also solubilize water in apolar solvents and they may form so-called reverse micelles.[1–3,9–14] Like normal, aqueous micelles, reverse micelles affect reaction rates and equilibria. The rates of ionic reactions are typically sensitive to solvent composition,[15] and the aqueous interiors of "water-pool" reverse micelles provide reaction media that are distinct from bulk, organic solvents.[13,14] However, solutions of ionic surfactants in apolar solvents may also contain ion pairs or small clusters with waters of hydration.

Association colloids affect reaction rates of bimolecular reactions by concentrating the reactants into small volumes.[1,16,17] This effect is absent in spontaneous, unimolecular reactions, and it is easier to treat association colloids quantitatively. We have examined the unimolecular decarboxylation of 6-nitrobenzisoxazole-3-carboxylate ion (6-NBIC)[13,14,18,19] and the hydrolysis of the 2,4-dinitrophenylphosphate dianion (DNPP^{2-})[20] in solutions of quaternary ammonium bromides in wet dichloromethane. These reactions are faster in aprotic, organic solvents than they are in water[21,22] and are accelerated by cationic surfactants in both water and CH_2Cl_2.[16,17] The reactions are also accelerated by hydrophobic quaternary ammonium salts which should form ion pairs or clusters rather than micelles, but the reactions in CH_2Cl_2 and ammonium salts are inhibited by the addition of water.[14,16]

Systematic studies using bimolecular reactions are scarce, probably because of the difficulty in the analysis of the data. In fact, as outlined above, there are three possible sites for the solubilization of the species, depending on their hydrophobic–hydrophilic nature. A quantitative analysis of a bimolecular reaction should take into account the partition of both reactants between the three possible microcompartments. In the literature there are some investigations of bimolecular reactions in reverse micelles, but they involve two neutral molecules.[23,24] In our present investigation we study bimolecular reactions of bromide

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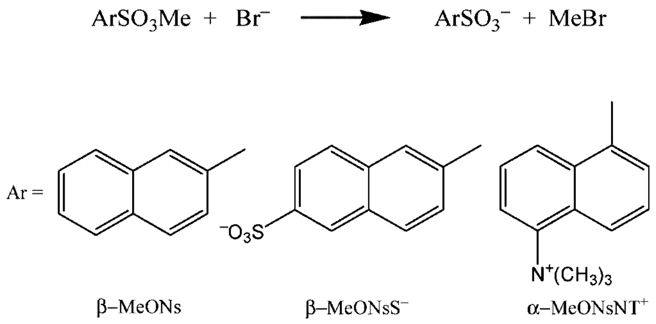
anions with substrates of different charge types (neutral, anionic, or cationic). In fact, we examine S_N2 reactions of Br^- with neutral methylnaphthalene-2-sulfonate (β-MeONs), with its anionic 6-sulfonate derivative (β-MeONsS⁻) and with cationic methyl-5-*N*,*N*,*N*,trimethylammonium naphthalene-1-sulfonate (α-MeONsNT⁺). The counterions associated with β-MeONsS⁻ are Na^+ or the lutidinium cation, and the counterion associated with α-MeONsNT⁺ is trifluoromethanesulfonate (triflate) (Scheme 1).



Scheme 1. Reaction of Br^- with β-MeONs, β-MeONS⁻, α-MeONsNT⁺.

The reaction of β-MeONs in water has been extensively investigated, and it is accelerated by cationic micelles,[25–27] and the rate effects are treated quantitatively in terms of the pseudophase models.[16,17,25–27] The onium salts used here are cetyltrimethylammonium bromide (CTABr), cetyltripropylammonium bromide (CTPABr) and tetra-*n*-butylammonium bromide (TBABr). All of these salts are moderately soluble in CH_2Cl_2 (not completely dry) and their solutions tolerate H_2O, but CTPABr and TBABr tolerate water only to a limited extent.

Results and Discussion

Reaction in Water

Rate constants for the spontaneous hydrolyses of β-MeONs, β-MeONsS⁻ and α-MeONsNT⁺ and rate constants for their reaction with Br^- are shown in Table 1, where k_{H_2O} and k_{Br} are first- and second-order rate constants, respectively. Values for β-MeONsS⁻ and β-MeONs are from the literature.[27] The value of the second-order rate constants for the reaction of α-MeONsNT⁺ with Br^- is calculated from the linear regression analysis of the experimental values of k_{obs} in NaBr, where $[Br^-] = 0.05–0.2$ M. The hydrolysis of α-MeONsNT⁺ is faster than that of β-MeONs by a factor of ca.3 and its reaction with Br^- is faster than that of β-MeONs by a factor of ca. 5. The higher reactivity of α-MeONsNT⁺ has to be related to its positive charge rather than to the position of the methylsulfonate group (α and not β) because the second-order rate constant for the reaction of α-MeONs with Br^- is 8.5×10^{-5}°$\mathrm{M}^{-1}\,\mathrm{s}^{-1}$, which is quite similar to the value of β-MeONs.[28]

Table 1. Rate constants for the reaction of water and Br^- with β-MeONs, β-MeONsS⁻, and α-MeONsNT⁺.[a]

	$10^5\,k_{H_2O}$ [s^{-1}]	$10^5\,k_{Br}$ [$M^{-1}\,s^{-1}$]
β-MeONs	1.25[b]	8.00[b]
β-MeONsS⁻[c]	2.30[b]	10.0[b]
α-MeONsNT⁺	3.89	41.5

[a] At 25.0 °C with 10^{-4} M substrate. [b] Ref.[27] [c] both Na^+ and Lu^+ as counterions give the same value of k_{obs}.

Reactions of β-MeONs and β-MeONsS⁻ with Br^- are accelerated by aqueous micelles of CTABr. Data for k_{obs} for these two substrates[25–27] are shown in Figure 1, together with values for k_{obs} for the reaction of α-MeONsNT⁺ with Br^- in aqueous micelles of CTABr. Values for k_{obs} for the reactions of β-MeONs and β-MeONsS⁻ with Br^- are corrected for the minor contribution from the reaction with water, measured in cetyltrimethylammonium methanesulfonate (CTAOMs, with a nonreactive counterion), as specified in the literature. Values for k_{obs} for the reactions of β-MeONs and β-MeONsS⁻ with Br^- increase sharply, and then tend toward limiting values, when substrates are fully bound in micelles. The kinetic data have been treated quantitatively by the use of the pseudophase model.[16,17,27] The first-order rate constant, k_{obs}, with respect to the substrate, S, is given by Equation (1):

$$k_{obs} = \frac{k_w[Nu_W^-] + k_M K_S\,[Nu_M^-]}{1 + K_S\,[D_n]} \tag{1}$$

where k_M (s^{-1}) is a second-order rate constant obtainedby writing the concentrations as the mole ratio of the nucleophile to the micellized surfactant (D_n), and K_s is the association constant for the substrate S; subscripts W and M denote the aqueous and micellar pseudophases, respectively

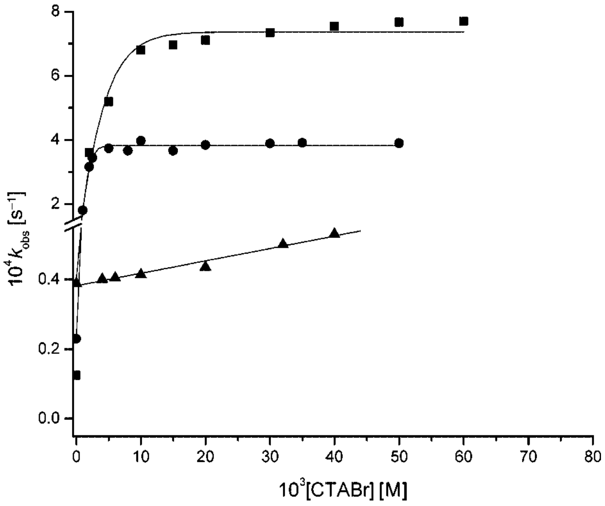


Figure 1. Reaction of β-MeONs (■), β-MeONS⁻ (●), and α-MeONsNT⁺ (▲) with Br^- in CTABr in water. For β-MeONs and β-MeONS⁻ values of k_{obs} are corrected for the minor contribution of the reaction with water, and lines are fitted to Equation 1;[27] for α-MeONsNT⁺ values of k_{obs} are not corrected for the contribution of the reaction with water, and the line is only to guide the eyes.

and quantities in square brackets are molarities in terms of total solution volume. Provided that the reaction is wholly in the micellar pseudophase, Equation (1) becomes Equation (2)

$$k_{\mathrm{obs}} = k_{\mathrm{M}}[\mathrm{Nu}^{-}_{\mathrm{M}}]/[\mathrm{D_n}] \quad (2)$$

where k_{M} (s^{-1}) is a second-order rate constant obtained by writing the concentrations as the mole ratio of the nucleophile to the micellized surfactant. Introduction of the anionic sulfonate moiety into β-MeONs affects the values for k_{M} for reactions in micelles: they are decreased by the 6-SO_3^- substituent by a factor of ca. 2 in CTABr.[27] Data in Figure 1 also show the reactions of α-MeONsNT$^+$ with Br$^-$. Values for k_{obs} for the reactions of α-MeONsNT$^+$ with Br$^-$ are not corrected for the contribution of the reaction with water. Values of k_{obs} for the reactions of α-MeONsNT$^+$ with water were measured in CTAOMs, and, unlike the case of β-MeONs and β-MeONsS$^-$, no surfactant effect was observed: the value of k_{obs} is the same as it is in pure water, at various concentrations of CTAOMs. Data for the reactions of α-MeONsNT$^+$ with Br$^-$ show that this reaction is practically unaffected by aqueous micelles of CTABr. Increases in k_{obs} are small, and are caused by the increase in bromide ion concentration as CTABr is added. In fact, they are similar to the changes due to the addition of NaBr, and in particular, the increases in k_{obs} with [CTABr] are almost linear. The different behaviour of α-MeONsNT$^+$ relative to that of the two other substrates, both in CTAOMs and in CTABr, may be due to the fact that it does not interact with the aqueous cationic micelle; we may suppose that it is located in the bulk water where it reacts with the water itself, or with bromide ions located in the bulk water.

Conductivity in CH_2Cl_2

The conductivities of all the onium salts used in this work (CTABr, CTPABr, TBABr) have already been investigated in our previous papers.[13,14] We repeated the investigation, however, because we worked in slightly different conditions. In particular, we worked with water-saturated dichloromethane, and we also used different concentrations of the onium salts. In fact, we could not use dry CH_2Cl_2, because well-dried CH_2Cl_2 does not solubilize onium salts. Therefore, we used CH_2Cl_2 equilibrated with water at 25 °C. The water content in the CH_2Cl_2 was measured prior to the experiments using the Karl Fisher method, as reported in the experimental section, and the amount of water solubilized in CH_2Cl_2 at equilibrium is 1.88 g/L, which is reproducible and consistent with the literature data.[19] Our prior results and the results obtained here are similar and are consistent with the interpretation already given in previous papers.[13,14] In the absence of added water, the conductivity of all our salts increases approximately linearly with [onium salt]. The addition of water leads to different behaviours for the different onium salts, as shown in Figure 2.

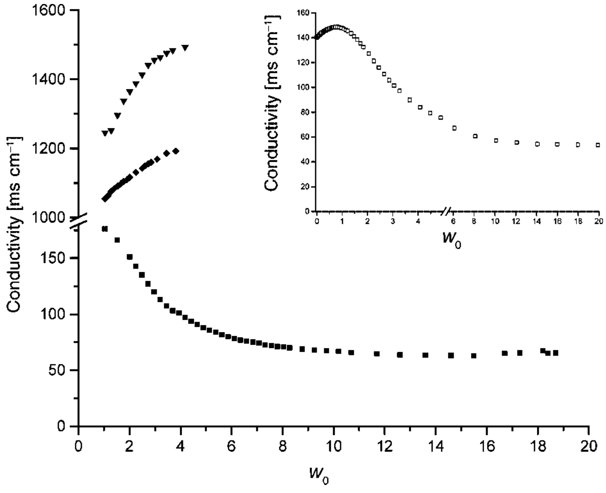


Figure 2. Effect of water on the conductivity in water-saturated CH_2Cl_2 in 0.1 M CTABr (■), CTPABr (♦), and TBABr (▼). In the inset: effect of water on the conductivity in dry CH_2Cl_2 in 0.09 M CTABr (□).[13]

Solutions of CTPABr and TBABr can tolerate only small amounts of water, and the addition of water increases the conductivity of these solutions, as shown in Figure 2: these data suggest that water breaks up ion clusters of CTPABr and TBABr. The usual model of the reverse micelle[1,29,30] is very reasonable when the headgroup is small, but it is difficult to see how bulky tetraalkylammonium salts can accommodate such structures, even in the presence of water. Our results are consistent with the presence of only ion pairs or clusters in solutions of CTPABr and TBABr, without the formation of reverse micelles at any concentration. On the other hand, solutions of CTABr tolerate relatively large amounts of water, probably by forming reverse micelles. A decrease in the conductivity of this solution is observed upon the addition of water (Figure 2). Although in our previous work[13] there was an initial increase in the conductivity of the solution up to a water content of ca. 0.06 M ($w_0 \approx 0.7$), a subsequent decrease in the conductivity was observed at greater concentrations of water (data in 0.09 M CTABr, shown in the inset in Figure 2). We probably cannot see any increase in the conductivity, because we used water-saturated CH_2Cl_2, with a water content of ca. 0.1 M. The decrease in conductivity of CTABr solutions, observed in both sets of data, is consistent with the formation of "water pool" micelles: in fact, these micelles are electrically neutral, and we expect the conductivity to decrease as they form. For solutions of CTABr in CH_2Cl_2, or similar solvents, added water will initially hydrate the ions, but, when the hydration shells are filled, additional water will exist as microdroplets, i.e., as a water pool, which is stabilized by surfactants at the surface. Under these conditions the conductivity of the solution decreases; NMR investigations show that under these conditions the chemical shift of water approaches that of bulk water,[13,14] and the behaviour of photochemical probes also comes closer to that of bulk water.[31]

Reactivities in CH_2Cl_2

Plots of k_{obs} against [onium salt] are linear and similar for the reactions of all three substrates. Data for CTABr are reported in Figure 3, and the results for CTPABr and TBABr are summarized in Table 2.

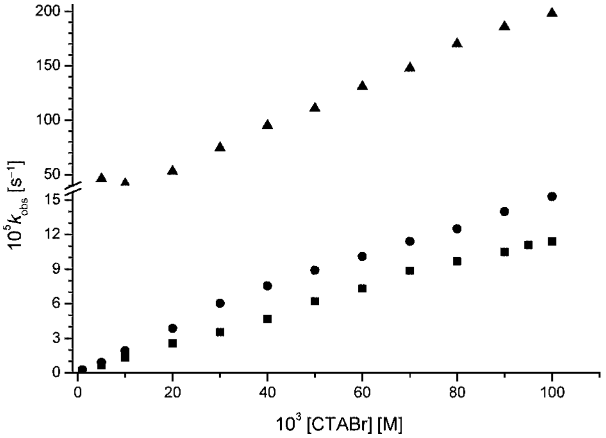


Figure 3. Reaction of β-MeONs (■), β-MeONS⁻ (●), α-MeONsNT⁺ (▲) with Br^- in CTABr in water-saturated CH_2Cl_2.

Table 2. Rate constants for reaction of Br^- with β-MeONs, β-MeONsS⁻, and α-MeONsNT⁺ in CH_2Cl_2 with CTPABr and TBABr.[a]

	β-MeONs		β-MeONsS⁻		α-MeONsNT⁺	
10^3 [onium salt], M	CTPABr	TBABr	CTPABr	TBABr	CTPABr	TBABr
5.0	1.45	1.83	1.63	1.98	–	96.9
10	2.99	3.69	3.53	4.02	170	124
20	6.04	7.47	7.16	9.27	180	194
30	9.38	11.5	10.5	14.6	215	269
40	13.3	16.2	15.5	20.1	290	346
50	16.6	20.8	18.9	25.7	336	408
60	20.0	26.4	23.0	29.1	406	468
70	24.6	31.4	28.3	35.7	450	535
80	28.6	37.7	33.6	41.8	527	596
90	34.5	42.2	38.1	48.6	568	656
100	39.0	43.9	44.8	51.1	616	757
120	48.1	–	55.5	–	–	–
150	–	72.4	–	82.4	814	1070
200	99.6	103	103	118	1206	1310

[a] Values of 10^5k_{obs} [s^{-1}], at 25.0 °C with 10^{-4} M substrate.

Reactions of Br^- are much faster in CH_2Cl_2 than they are in water. Reaction rates correlate with increases in the conductivity with [onium salts], and both reactivity and conductivity increase as the bromide ion content increases. Rate constants for the reaction with CTABr are similar for β-MeONs and β-MeONsS⁻, while they are higher for α-MeONsNT⁺. The positive charge of α-MeONsNT⁺ should increase the probability of an encounter with Br^-. Rates also vary significantly with the nature of the onium salts, and the order is TBABr > CTPABr > CTABr. Relative reactivities for the three substrates with CTPABr and TBABr are similar to those in CTABr (Table 3). In fact, ratios of the k_{obs} values at 0.1 M [onium salt] for α-MeONsNT⁺ and for β-MeONs are ca. 15–17 in all the onium salts. From the data in water it is evident that α-MeONsNT⁺ is an inherently more reactive substrate, but in water the ratio of the second-order reaction rates for the reaction of α-MeONsNT⁺ with Br^- to that of β-MeONs with Br^- is smaller: ca. 5 (Table 1). Catalytic effectiveness correlates with conductivity in CH_2Cl_2. Big-head onium salts are the best catalysts, in fact TBABr and CTPABr have higher rate constants than CTABr, and they also have higher conductivities. Plots of k_{obs} against the conductivity for the reaction of β-MeONs with Br^- in 0.1 M onium salts in CH_2Cl_2 are linear if plotted against conductivity of 0.1 M onium salts in CH_2Cl_2 (same solution used for kinetic experiments), with $R^2 = 0.9996$. Data for the other substrates also show a linear plot, with good correlations, and $R^2 = 0.9999$ for β-MeONsS⁻ and $R^2 = 0.9970$ for α-MeONsNT⁺ (Table 3).

Table 3. Values of the conductivity of β-MeONsS⁻ and α-MeONsNT⁺ in solutions of 0.1 M CTABr, CTPABr and TBABr in CH_2Cl_2 at 25 °C, and values of k_{obs} for the reactions of Br^- with β-MeONsS⁻ and α-MeONsNT⁺.

	Conductivity [mS cm^{-1}]	β-MeONsS⁻ [a]	α-MeONsNT⁺ [a]
CTABr 0.1 M	0.176	15.3	198
CTPABr 0.1 M	1.054	44.8	616
TBABr 0.1 M	1.245	50.7	757

[a] Values of 10^5k_{obs} [s^{-1}], at 25.0 °C with 10^{-4} M substrate.

This headgroup effect is also evident in the decarboxylation of 6-NBIC[13] and in the hydrolysis of the 2,4-dinitrophenylphosphate dianion (DNPP^{2-}) where the rates in solutions of quaternary ammonium salts in CH_2Cl_2 increase with increasing bulkiness of the headgroup (from CTABr to CPABr and also CTBABr, i.e. cetyl tri-*n*-butylammonium bromide).[20] Also for these two monomolecular reactions, catalytic effectiveness correlates with conductivities.[13,14,20] Because ion-pairing decreases the nucleophilicity of Br^-, big-head ammonium bromides are the best catalysts since these substrates react with ion pairs, or possibly clusters. Ion-pairing is thought to be stronger with smaller headgroups, thus decreasing the rate of the reaction.

Effect of Water

The addition of water inhibits reactions of Br^- with all three substrates. Data for the reaction of β-MeONs with Br^- in CTABr, CTPABr, and TBABr are shown in Figure 4 and the data for the reaction of β-MeONsS⁻ and α-MeONsNT⁺ with Br^- in CTABr, CTPABr and TBABr are listed in Table 4. Clusters or ion pairs that are present at low water content levels are evidently more effective catalysts than hydrated clusters or water-pool reverse micelles. We could add only small amounts of H_2O to solutions of TBABr and CTPABr, but solutions of CTABr are more tolerant. We used 0.2 M CTPABr and TBABr in order to study a larger range of w_0, Figure 4.

Table 4. Values of k_{obs} at various w_0 in 0.1 M CTABr, 0.2 M CTPABr and 0.2 M TBABr in CH_2Cl_2 for the reaction of Br^- with β-MeONsS$^-$ and α-MeONsNT$^+$.[a]

	CTABr		CTPABr		TBABr	
w_0	β-MeONsS$^-$	α-MeONsNT$^+$	β-MeONsS$^-$	α-MeONsNT$^+$	β-MeONsS$^-$	α-MeONsNT$^+$
0.627	–	–	10.3	121	–	–
0.766	–	–	9.85	106	–	–
0.855	–	–	–	–	11.7	131
0.905	–	–	9.38	95.8	–	–
0.994	–	–	–	–	11.4	117
1.04	–	–	8.80	90.1	–	–
1.13	–	–	–	–	11.0	106
1.33	1.53	19.8	7.82	76.2	10.0	96.0
1.61	1.47	15.4	7.02	68.9	9.15	82.0
1.89	1.34	14.0	–	–	8.33	73.8
2.01	–	–	6.12	56.9	–	–
2.16	1.26	12.7	–	–	7.05	61.8
2.44	1.22		–	–	–	–
2.72	1.19	11.4	–	–	–	–
3.00	1.13	–	–	–	–	–
3.27	1.09	10.9	–	–	–	–
4.11	1.02	10.5	–	–	–	–
5.49	0.983	9.78	–	–	–	–
6.88	0.972	9.36	–	–	–	–
9.66	0.969	8.93	–	–	–	–
12.4	0.961	8.79	–	–	–	–
15.2	0.977	8.57	–	–	–	–

[a] Values of $10^4 k_{obs}$ [s^{-1}], at 25.0 °C with 10^{-4} M substrate.

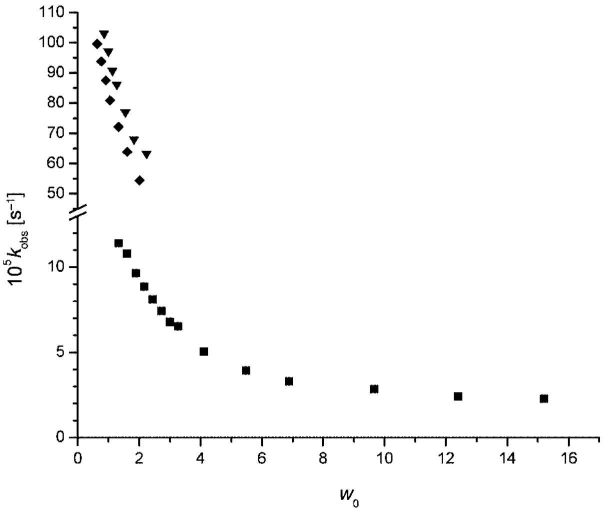


Figure 4. Values of k_{obs} for the reaction of Br^- with β-MeONs in CH_2Cl_2 against w_0 in CTABr 0.1 M (■), CTPABr 0.2 M (♦) and TBABr 0.2 M (▼).

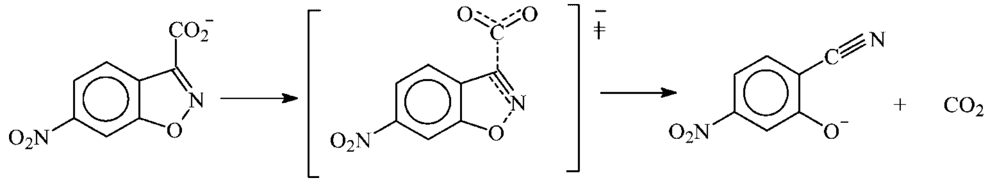
As shown in Figure 4 for the reaction of β-MeONs and in Table 4 for the other two substrates, k_{obs} values for all three substrates in solutions of 0.1 M CTABr initially decrease almost linearly and then become approximately constant at $w_0 \approx 6$. Ratios of the values of k_{obs} at the plateau ($w_0 > 6$) and values of k_{obs} without any added water are ca. 0.6 for β-MeONsS$^-$, ca. 0.2 for β-MeONs and ca. 0.4 for α-MeONsNT$^+$ (Figure 4 and Table 4).

Reactions with 0.2 M CTPABr and 0.2 M TBABr are also inhibited by H_2O, but the water concentration was limited to ca. 0.4 M (ca. $w_0 = 2$). The value of k_{obs} decreases almost linearly, as in the first part of the plot for CTABr (Figure 4).

In CTABr the change in slope at $w_0 \approx 5$–6 has also been observed for the decarboxylation of 6-NBIC:[14] the similar behaviour for two very different reactions indicates a change in the aggregate structure of CTABr.

Mechanistically, decarboxylation of 6-NBIC (Scheme 2) and S_N2 reactions of Br^- are very different and the rate increases with the latter. Increases in the reaction rate in solutions of CTABr, CTPABr and TBABr could be a result of an increase in [Br^-], but H_2O similarly inhibits both reactions.

For example, decarboxylation in a variety of cationic surfactants is initially inhibited by the addition of H_2O to CH_2Cl_2,[14,18,19] but k_{obs} levels off at $w_0 \approx 5$, as do the S_N2 reactions with Br^-. Hydrogen bonding donors inhibit both decarboxylation and bimolecular reactions of anions by stabilizing the initial states,[15] as for the reactions in solutions of CTABr in CH_2Cl_2, but with w_0 in the range 5–6, values of k_{obs} become independent of [H_2O]. The similarities in the effects of H_2O on two mechanistically different reactions should be related to a change in the reaction environments at a particular value of w_0. In moist CH_2Cl_2, onium salts exist as ion pairs or clusters, which are hydrated to extents dependent on the availability of H_2O. Ionic hydration probably increases with the addition of H_2O to CH_2Cl_2, which inhibits decarboxylation and S_N2 reactions of Br^-. Above some limit, e.g., $w_0 \approx 6$, new structures appear, which are probably "water-pool" reverse micelles, and additional H_2O enters their interiors. As already mentioned above, these structures should not form with quaternary ammonium ions that have bulky headgroups, e.g., Pr_3N^+ or Bu_4N^+ and CTPABr and TBABr only tolerate limited H_2O in CH_2Cl_2, where $w_0 \approx 2$, without phase separation.



Scheme 2. Decarboxylation of 6-NBIC.

There is physical evidence for the existence of both "interfacial water" that is in contact with surfactant and "bulk-like" water, depending on w_0 in AOT-derived micelles and in cationic reverse micelles.[19] For example, ^1H NMR chemical shifts of H_2O in solutions of CTABr in CD_2Cl_2 or $CDCl_3$ increase towards values that are typical for bulk water as w_0 is increased, and chemical shifts of NCH_3 and $CH_2(I)$ correspondingly decrease. Chemical shifts provide information on average structures in rapidly equilibrating systems, but infrared spectroscopy distinguishes between different types of water in reverse micelles. The IR spectrum of H_2O in CTABr–CH_2Cl_2 shows that some H_2O is free in CH_2Cl_2 and independent of w_0. The amount of H_2O intimately associated with CTABr increases sharply with increasing w_0, up to $w_0 \approx 6$, and then increases slowly, and linearly, with w_0.[19] The break occurs at almost the same value of w_0 as the breaks in plots of k_{obs} against w_0 for both decarboxylation and S_N2 reactions of Br^-. It appears that with increasing H_2O, $w_0 \approx 6$, "water-pool" reverse micelles form, and the rates of decarboxylation and S_N2 reactions become kinetically independent of w_0.

With $w_0 > 6$, k_{obs} of β-$MeONsS^-$ is larger than that of β-MeONs, by a factor of ca. 4.3, probably because the low solubility of the anionic substrate in CH_2Cl_2 drives it into the interface formed by the reverse micelles, in proximity with Br^-, unlike β-MeONs, which probably remains, more in the bulk solvent. At $w_0 > 6$, k_{obs} for the cationic substrate α-$MeONsNT^+$ is always greater than the others, but it is more water-inhibited than β-$MeONsS^-$. For all substrates the reaction with 0.1 M CTABr in these conditions is independent of $[H_2O]$: it appears that with constant [CTABr] reactivity is not significantly affected by a change in the average micellar size induced by an increase in w_0. Above the limiting value of $w_0 \approx 6$ increases in w_0 do not inhibit reactions of Br^- with the three substrates. These generalizations are based on data with constant [CTABr] and variable $[H_2O]$, and we note that our experimental conditions are limited by the solubilities of CTABr and H_2O in CH_2Cl_2.

Experimental Section

Materials: CH_2Cl_2 (BDH) was distilled to remove any EtOH present, and then equilibrated with water by the addition of excess deionized water (conductivity = 0.085 μS).The mixture was kept at 25 °C for 12 h, transferred to a separatory funnel, and the water was removed. The CH_2Cl_2 was placed in a sealed container in the dark at 25 °C. CTABr and TBABr are from Fluka, and CTPABr was prepared previously.[13] The salts were crystallized as described earlier[13] and dried to constant weight before use. β-MeONs and β-$MeONsS^-$ were initially prepared and converted to α-methyl-5-dimethylaminonaphthalenesulfonate by the reaction with CH_3OH for 2 h. The product was then it was quaternized by the reaction with methyltrifluoromethanesulfonate at room temp. for 24 h in dry CH_2Cl_2 in the presence of molecular sieves. The crude product was crystallized from ethyl ether/ethyl acetate, and a solid with m.p. 129 °C was obtained in 75% yield. The recrystallized product was stored in the dark, at 4 °C, under a N_2 atmosphere. ^1HNMR (200 MHz, CD_3OD, room temp.): $\delta = 3.79$ (s, 3 H, CH_3), 4.07 (s, 9 H, NCH_3), 7.89–9.10 (m, 6 H, aromatic).

Kinetics: The decreasing absorbances of β-MeONs at 326 nm, β-$MeONsS^-$ at 330 nm, and α-$MeONSNT^+$ at 320 nm were followed with HP8452 or Shimadzu 160A spectrophotometers at 25.0 ± 0.1 °C. Substrates were added in CH_2Cl_2 (for charged substrates a few drops of MeOH were added to obtain homogeneous solutions in CH_2Cl_2).

Conductivity: The conductivity was measured at 25 °C with an Analytical Control Model 120 micro Processor Conductivity Meter. The cell was kept closed during measurements.

Water Content in CH_2Cl_2: The water content was measured in water-saturated CH_2Cl_2 by the Karl Fisher method, with a Metrohm mod 684 KF Coulometer, Series 01, which directly reports values of water content in μg. In CH_2Cl_2, water content is 1.88 g/L; in 0.1 M CTABr water content is 2.44 g/L; in 0.2 M CTPABr water content is 2.26 g/L and in 0.2 M TBABr water content is 3.08 g/L.

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