compressibility goes to zero there, for instance. (2) Glass transitions are not anticipated by thermodynamic anomalies in the liquid as T_g is approached from above, in contrast to the situation in water where a variety of anomalies[1] anticipate the approach to T_s. (3) According to the stability limit conjecture,[3,6] the gel is mechanically unstable so that any structural relaxation that can occur on the experimental time scale will be toward a more stable phase (i.e. ice), rather than toward equilibration within amorphous phase space.

Despite these differences, the formation of a gel in a rapid-cooling experiment should be like a glass transition in some respects. In particular, the heat capacity of water, which increases rapidly as $T \rightarrow T_s$ as a consequence of the rapid structural change (e.g., growth of the low-density domains[4,5]), should drop sharply to a value similar to that of ice when the structural relaxation time exceeds the experimental time scale and structural change is arrested, just as at a glass transition. Angell and Tucker[25] have discussed this point in some detail.

The experimental evidence, from studies of cooling liquid water[1,15] and of heating ASW,[18] suggest that between about 160 and 232 K any structural relaxation that occurs in the amorphous state of water leads to the formation of ice. There is no evidence for the existence of an internally equilibrated metastable amorphous state in that temperature range. Given this "stability gap", there is no reason to expect that the structure toward which water tends as $T \rightarrow T_s$ is closely related to ASW. The evidence on this point is not yet conclusive because the rapidly quenched samples are contaminated with the hydrocarbon cooling fluid.[15]

The debate concerning the possible continuity of states between ASW and liquid water has focused[1,14,16,25,26] on attempts to resolve the "entropy paradox". Plausible extrapolations to estimate the entropy that liquid water would have if it could be equilibrated in the "stability gap" become less than the entropy of ice above 160 K. It is important to recognize in this connection that attempts to estimate an entropy by integrating the heat capacity along an arbitrary irreversible path do not resolve this paradox.

The evidence that most measures of structural relaxation times in supercooled water are tending to diverge[1,2,3] at T_s, rather than at T_g, is not explained by the continuity of states hypothesis. Figure 3 shows plots of $\eta^{-5/8}$ and λ_{H^+} against T, which is intended to show that the extrapolation to zero at $T_s \simeq 227$ K, particularly the linear extrapolation of the precise λ_{H^+} results that extend to 242 K, is more convincing than would be any extrapolation to zero at $T_g < 160$ K.

We therefore take the view that liquid water forms a rigid gel at $T_s \simeq 227$ K, if it does not freeze above T_s, and it is the structure of this gel rather than the structure of ASW that should serve as a model for the underlying structure and properties of liquid water. The structure of the gel is as yet unknown, and it may turn out to be the same as that of ASW. However, in view of the stability limit conjecture[3,6] and the recent models of the structure of supercooled water,[4,5,26] it is likely that the gel contains extensive domains of some low-density clusters immersed in a more dense background random network and is, thereby, distinguishable from ASW. For example, the frozen in density fluctuation of the gel should scatter light and make it opaque.

The proton mobility in the gel at T_s may be similar to that in ice. In HF-doped ice[24] λ_{H^+} is about 10 Ω^{-1} cm^2 mol^{-1} at −10 °C, which corresponds to the extrapolated λ_{H^+} in water at about −42 °C from Figure 3. The rate-limiting factor for proton migration in the gel, and in supercooled water, is probably the concentration of the kind of defects that limit proton migration in ice.[24] This conclusion is in contrast to most models of proton transfer in water,[8,9] which postulate that the rate-limiting step is a structural relaxation process (e.g., the reorientation of a water molecule adjacent to the hydronium ion) and therefore should have a similar temperature dependence to other measures of structural relaxation times in water. The Walden product $\eta\lambda^0_{H^+}$ doubles between +25 and −25 °C, whereas $\eta\lambda^0_{Cl^-}$, $\eta\lambda^0_{K^+}$, η/τ_0 (τ_0 is the reorientational correlation time), and ηD (D is the self-diffusion coefficient) are relatively constant.[2]

Registry No. HCl, 7647-01-0; H$^+$, 12408-02-5; water, 7732-18-5.

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Kinetic Behavior of Cetyltrimethylammonium Hydroxide. The Dehydrochlorination of 1,1,1-Trichloro-2,2-bis(*p*-chlorophenyl)ethane and Some of Its Derivatives

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The dehydrochlorination of 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (DDT), 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane (DDD), and 1-chloro-2,2-bis(*p*-chlorophenyl)ethane (DDM) with hydroxide ion was studied in the presence of hexadecyltrimethylammonium hydroxide (CTAOH) micelles at 25.0 °C. The experimental results clearly deviate from the theoretical behavior expected by the pseudophase-ion-exchange model and can be explained by considering an additional reaction pathway across the micellar boundary. This additional reaction pathway in which hydroxide ion in the aqueous phase reacts directly with the organic substrate in the micelle is probably of a phase-transfer catalysis type.

Introduction

Although in the last few years significant progress has been made in the quantitative treatment of micellar catalysis,[1-10] we are still far from a complete understanding of the different processes involved in these phenomena. Indeed, at high counterion

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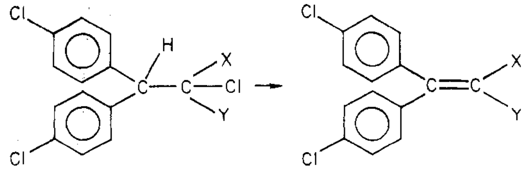
Scheme I



DDT, X = Y = Cl
DDD, X = Cl, Y = H
DDM, X = Y = H

DDE, X = Y = Cl
DDMU, X = Cl, Y = H
DDNU, X = Y = H

concentration[11] and in the presence of reactive counterion type micelles[12-15] several reports of apparent failures of the pseudophase model for kinetics of micellar-catalyzed reaction have appeared in the literature.

It is well accepted and generally agreed that micellar catalytic effects in bimolecular reactions are observed when there is a favorable partition of the substrate between the aqueous and micellar phases. Thus, the rate increase is explained in terms of an increase of the concentration of the reagents in the micellar phase. Besides this concentration effect, changes in reactivity of the substrate in the two pseudophases are also an important part of the rate increase and/or decrease observed.

Basically, all the kinetic treatments of the rate constant–surfactant profile in bimolecular reactions (A + B → products) are derived from eq 1, where the subscripts w and m refer to the

$$\text{rate} = k_{2\text{w}}[\text{A}]_\text{w}[\text{B}]_\text{w} + k_{2\text{m}}[\text{A}]_\text{m}[\text{B}]_\text{m} \qquad (1)$$

aqueous and micellar phases. Equation 1 is consistent with a phase separation model, with the chemical reaction occurring in the aqueous phase (first term in eq 1) or in both phases.

The concentration of reagents in each phase will depend on the partition coefficients for neutral species and, of course, on the ion-exchange phenomena for reactions involving ions.[10]

It is important to note that a phase separation model, as the one used in the kinetic treatment, assumes a closed thermodynamic system since it involves partitioning of the substrate and ion-exchange phenomena, which on a final analysis are dependent on a limited number of sites. The failure of the pseudophase model observed at high counterion concentration[11] and in the presence of reactive counterion type micelles[12-15] has been explained by Bunton, Romsted, and Savelli[12] in terms of an additional reaction pathway across the micellar boundary at the shear surface between the Stern and Gouy–Chapman layers of the micelle.

In the present work, we would like to report the dependence of this new reaction pathway on surfactant and hydroxide ion concentration in the presence of hexadecyltrimethylammonium hydroxide (CTAOH). Since the reactions chosen for this purpose were the dehydrochlorination of 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (DDT), 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane (DDD), and 1-chloro-2,2-bis(*p*-chlorophenyl)ethane (DDM) with hydroxide ion (Scheme I), CTAOH behaves as a reactive counterion surfactant.

The main advantage of DDT, DDD, and DDM as substrates for testing the pseudophase model is their low solubility in water,[16] a fact that allows a somewhat simpler kinetic analysis of the system[11] by eliminating the possibility of reactions in the aqueous phase, which might obscure other processes across the interfacial boundary. Our results give strong support to the presence of this third reaction pathway as a normal component in micellar catalysis.

Experimental Section

The compounds 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (DDT) and 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane (DDD) were purchased from Aldrich Chemical Co., and their purity was found to be satisfactory by thin-layer-chromatographic, UV, and IR analysis. The compound 1-chloro-2,2-bis(*p*-chlorophenyl)ethane (DDM) was prepared by a slight modification of a previously described procedure[16] and crystallized several times from ethanol, mp 51–51.5 °C (lit.[17] mp 51–51.5 °C). Purification of cetyltrimethylammonium bromide has been described.[18]

Solutions of CTAOH were prepared by treating CTABr with a 50-fold excess of Orzelith ESB-32 ion-exchange resin in the hydroxide form. In all experiments CO_2-free water was used and the manipulations of CTAOH were carried out under a N_2 atmosphere. The absence of bromide ion in the stock solutions of CTAOH was confirmed by treatment of the acidified solutions with silver nitrate. The stock solutions thus prepared were stored in a refrigerator.

Rates of dehydrochlorination of DDT, DDD, and DDM were determined following (Shimadzu UV-210-A spectrophotometer) the appearence of 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene (DDE) at 260 nm, 1-chloro-2,2-bis(*p*-chlorophenyl)ethylene (DDMU) at 257 nm, and 1,1-bis(*p*-chlorophenyl)ethylene (DDNU) at 252 nm, respectively.

The temperature for the kinetic runs was maintained at 25.0 ± 0.1 °C by using a water-jacketed cell compartment. Individual pseudo-first-order rate constants, $k_{\psi\text{m}}$, were obtained from linear plots of ln $(A_\infty - A_t)$ vs. time. All of these plots were linear for at least 90% of the reaction, and the correlation coefficients were greater than 0.99.

The kinetic and physicochemical behavior of CTAOH prepared as described above was identical with that of a sample of the same detergent prepared by the method reported by Bunton et al.[13] The critical micelle concentration (cmc) of CTAOH was determined by surface tensiometry, the measurements being made at 25.0 °C under a nitrogen atmosphere by means of a Fisher Model 21 semiautomatic tensiometer. Ten-milliliter aliquots of the solutions were placed in a Petri dish with a diameter of 6 cm and the final value of the surface tension was the average of three independent measurements. A value of 8.9×10^{-4} M (lit.[13] 8.6×10^{-4} M) was obtained for the cmc of CTAOH from the inflection point of a surface tension vs. log [CTAOH] plot which showed no minima.

Conductivity measurements, at 25 °C under N_2, did not show a well-defined break and some curvature of plots of log (specific conductivity) vs. log [CTAOH] were observed at the $(1.5\text{–}2.5) \times 10^{-3}$ M surfactant concentration but, as reported by Bunton, the "break" is so ill-defined that it cannot be used as measurement of the cmc.

Comparison of the S_1 values (Evans treatment)[13] of CTAOH with those of CTABr, $1000\,(S_1^{\text{CTAOH}} - S_1^{\text{CTABr}}) = 115$, which agrees with the theoretical value (119) expected from the differences in ionic conductivity of hydroxide and bromide ions, further substantiates the purity of our CTAOH samples. Using the conductivity measurement and Evans treatment, we obtained a value of 0.4 for β; this value somewhat disagrees with that of 0.6 reported by Bunton.[13] However, considering that the experimental data for S_2 were taken in the $(2.0\text{–}20.0) \times 10^{-3}$ M range, the value of 0.4 agrees well with that theoretically expected using a binding constant[13] of 55 M^{-1}. Besides, a low value of the binding constant results in a change of β in the experimental range of concentration which may be responsible for the discrepancy of our value from that reported by Bunton and surely reinforces Bunton's doubts about the validity of the application of Evans

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treatment in ionic surfactants with counterions of low binding constant.[13]

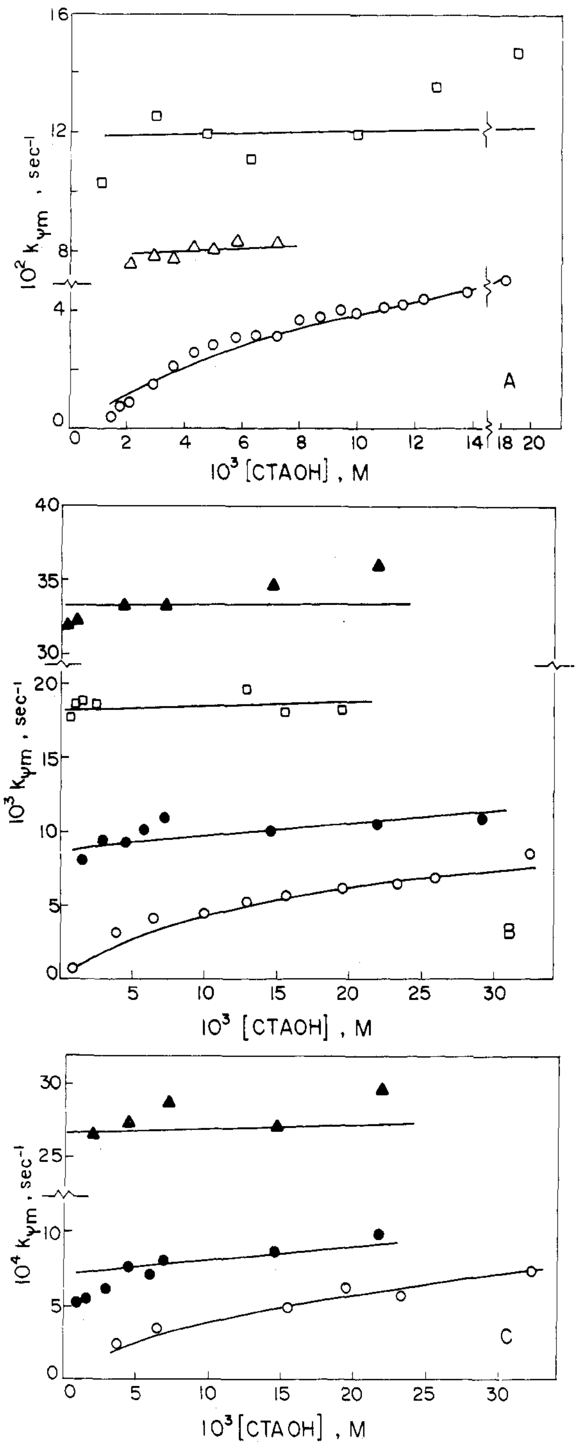

Figure 1. Plot of the observed pseudo-first-order rate constant vs. surfactant concentration at constant added hydroxide ion. A: DDT, $[OH^-]$ = 0.00 (○), 3.60×10^{-2} (△), 1.84×10^{-1} (□) M. B: DDD, $[OH^-]$ = 0.00 (○), 1.86×10^{-2} (●), 1.85×10^{-1} (□), 3.24×10^{-1} (▲) M. C: DDM, $[OH^-]$ = 0.00 M (○), 1.86×10^{-2} (●), 3.24×10^{-1} (▲) M.

Results and Discussion

The dehydrochlorination reactions of DDT, DDD, and DDM with hydroxide ion in aqueous solutions of CTAOH were studied with varying concentrations of surfactant and base. When no hydroxide was added to the system, the pseudo-first-order rate constant was found to increase with increasing surfactant concentration; in the presence of a constant concentration of added hydroxide ion, the pseudo-first-order rate constant was essentially independent of the increasing surfactant concentration (Figure 1A–C). When the surfactant concentration was kept constant, the pseudo-first-order rate constant increased with increasing hydroxide concentration and a linear dependence of $k_{\psi m}$ on [NaOH] was observed at high concentration of hydroxide ion (Figures 2A–C).

TABLE I: Second-Order Rate Constants in CTAOH

[OH],[a] M	[CTAOH],[b] M	k_{2m},[c] M^{-1} s^{-1}	$k_{2m/w}$, M^{-1} s^{-1}
	DDT Substrate		
0.00		3.90×10^{-2}	9.01×10^{-2}
3.60×10^{-2}		3.45×10^{-2}	8.03×10^{-2}
1.84×10^{-1}		3.45×10^{-2}	7.97×10^{-2}
	1.46×10^{-3}	2.40×10^{-2}	7.05×10^{-2}
	3.81×10^{-3}	3.30×10^{-2}	5.55×10^{-2}
	1.42×10^{-2}	4.05×10^{-2}	7.00×10^{-2}
	DDD Substrate		
0.00		4.20×10^{-3}	3.00×10^{-2}
1.86×10^{-2}		4.80×10^{-3}	3.00×10^{-2}
1.85×10^{-1}		4.50×10^{-3}	3.00×10^{-2}
3.24×10^{-1}		4.50×10^{-3}	3.00×10^{-2}
	3.60×10^{-4}	3.00×10^{-3}	3.00×10^{-2}
	1.46×10^{-3}	3.90×10^{-3}	3.00×10^{-2}
	7.32×10^{-3}	4.50×10^{-3}	3.30×10^{-2}
	DDM Substrate		
0.00		3.90×10^{-4}	3.50×10^{-3}
1.86×10^{-2}		3.90×10^{-4}	3.00×10^{-3}
3.24×10^{-1}		5.10×10^{-4}	3.00×10^{-3}
	8.78×10^{-4}	3.00×10^{-4}	3.50×10^{-3}
	1.46×10^{-3}	3.00×10^{-4}	2.70×10^{-3}
	7.32×10^{-3}	3.00×10^{-4}	2.50×10^{-3}

[a] Variable concentration of CTAOH. [b] Variable concentration of hydroxide ion. [c] Taking $\bar{V}$ as 0.30.

The above results clearly deviate from the theoretical behavior expected by the pseudophase-ion-exchange model.[1-15] Thus, once the substrate is completely bound, the pseudo-first-order rate constant for reactive counterion surfactants should remain constant with increasing surfactant concentration. Moreover, addition of hydroxide ion to this system should cause no changes in the observed rates.

These discrepancies are not unprecedented. Bunton and coworkers[12] reported similar deviations and proposed an additional reaction pathway across the interfacial boundary; this proposal found support in our studies of the dehydrochlorination of DDT, DDD, and DDM with hydroxide ion in the presence of hexadecyltrimethylammonium bromide (CTABr) micelles.[11] Our suggestion of a phase-transfer catalysis as the additional reaction pathway corresponds to introducing a new kinetic term in eq 1, which describes a reaction pathway across the micelle–water interface.

$$k_{\psi m} = k_{2w}[OH^-]_w[DDT]_w + k_{2m}[DDT]_m[OH^-]_m + k_{2m/w}[OH^-]_w[DDT]_m \quad (2)$$

Starting from eq 2 one can easily derive[1-15] eq 3, which describes

$$k_{\psi m} = \frac{k_{2m}[OH^-]_w + \frac{k_{2m}}{\bar{V}} K_s [OH^-]_m}{1 + K_s C_D} + k_{2m/w}[OH^-]_t \quad (3)$$

the observed pseudo-first-order rate constant, $k_{\psi m}$, as a function of the total hydroxide ion concentration, $[OH^-]_t$. The terms k_{2m}, k_{2w}, and $k_{2m/w}$ refer to second-order rate constants in the micellar phase, in the aqueous phase, and in the micelle-water interfacial boundary, respectively. The subscripts w, m, and t in the concentration terms refer to the aqueous and micellar phases and to the total stoichiometric concentration. K_s represents the binding constant for the organic substrate, C_D the concentration of micellized detergent, which corresponds to the stoichiometric detergent concentration minus the cmc, and $\bar{V}$ the effective volume per mole of detergent.

Considering that the solubility of DDT in water at 25 °C is about 3×10^{-10} M[19] and that in the presence of 10^{-3} M CTAOH

TABLE II: Kinetic Parameters Obtained with the Theoretical Treatment of the Data

	CTABr[a]		CTAOH	
substrate	k_{2m}, M^{-1} s^{-1}	$k_{2m/w}$, M^{-1} s^{-1}	k_{2m}, M^{-1} s^{-1}	$k_{2m/w}$, M^{-1} s^{-1}
DDT	$(1.40 \pm 0.22) \times 10^{-2}$	$(1.27 \pm 0.66) \times 10^{-1}$	$(3.42 \pm 0.57) \times 10^{-2}$	$(7.42 \pm 1.20) \times 10^{-2}$
DDD	$(4.00 \pm 0.82) \times 10^{-4}$	$(5.00 \pm 1.83) \times 10^{-2}$	$(4.20 \pm 0.60) \times 10^{-3}$	$(3.04 \pm 0.12) \times 10^{-2}$
DDM	$(1.00 \pm 0.20) \times 10^{-4}$	$(2.40 \pm 0.75) \times 10^{-2}$	$(3.63 \pm 1.00) \times 10^{-4}$	$(3.03 \pm 0.41) \times 10^{-3}$

[a] Taken from ref 11.

a concentration of 10^{-5} M of DDT is readily solubilized, the K_s value can be estimated from $[DDT]_m/[DDT]_w = 1 + K_sC_D$ to be higher than 3×10^{-7} M^{-1}.

Using a solubility value of about 1×10^{-9} M for DDD[20] and 1×10^{-8} M for DDM,[21] one can estimate in a similar way K_s values higher than 10^6 and 10^5 M^{-1} for DDD and DDM, respectively. Since $K_sC_D \gg 1$ and the mole fraction of the organic substrate in the aqueous phase approaches zero, eq 3 can be simplified to eq 4.

$$k_{\psi m} = \frac{k_{2m}}{C_D\bar{V}}[OH^-]_m + k_{2m/w}[OH^-]_t \tag{4}$$

In order to use eq 4 we need to evaluate $[OH^-]_m$. This can be conveniently done by combining eq 5, which describes the binding

$$K_{OH} = [OH^-]_m/\{[OH^-]_w(C_D - [OH^-]_m)\} \tag{5}$$

of hydroxide ion in terms of mass action equilibrium, with the mass balance for hydroxide ion, $[OH^-]_t = [OH^-]_m + [OH^-]_w$. The resulting equation 6 can be used to calculate $[OH^-]_m$ as a function

$$K_{OH}[OH^-]_m^2 - (K_{OH}C_D + K_{OH}[OH^-]_t + 1)[OH^-]_m + K_{OH}C_D[OH^-]_t = 0 \tag{6}$$

of the total stoichiometric concentration of hydroxide ion, $[OH^-]_t$, C_D, and K_{OH}. A value of 55 M^{-1} for the binding constant of hydroxide ion was used to calculate the concentration of hydroxide ion in the micellar phase.[13]

Figures 1A–C and 2A–C show the results of the application of eq 6 to the experimental data. As can be seen, the theoretical curves obtained fit the data quite well. The values of k_{2m} and $k_{2m/w}$ obtained for the best fits of the experimental data are given in Table I. Inspection of this table shows that the values obtained for k_{2m} and $k_{2m/w}$ for each substrate are identical within experimental error, irrespective of the changing concentrations of surfactant and/or hydroxide ion. Average values of k_{2m} and $k_{2m/w}$ for CTAOH are given in Table II; for comparison purposes, k_{2m} and $k_{2m/w}$ values for CTABr[11] are also included.

Several trends can be observed in Table II. The reactivity of the polyhalogenated hydrocarbon pesticides, measured in terms of k_{2m} and $k_{2m/w}$ in either CTABr or CTAOH, increases as we go from DDM to DDD to DDT, a result which parallels the order observed in water–ethanol solutions.[22]

Although it is difficult to make comparisons of the second-order rate constants in the micellar pseudophases, k_{2m}, since they depend directly upon the estimation of the element of volume in which the reaction effectively occurs, which may well vary from CTABr to CTAOH, it seems that the latter is slightly more effective than CTABr in promoting the dehydrochlorination of DDM, DDD, and DDT. It is clear, however, that the main catalytic advantage of the micelle, as far as k_{2m} is concerned, is the increase in concentration of both the hydrophobic substrate and the hydrophilic reactive counterion in the micellar phase.

Table II also shows that the values of $k_{2m/w}$ for each substrate are practically the same with both surfactants. This result clearly

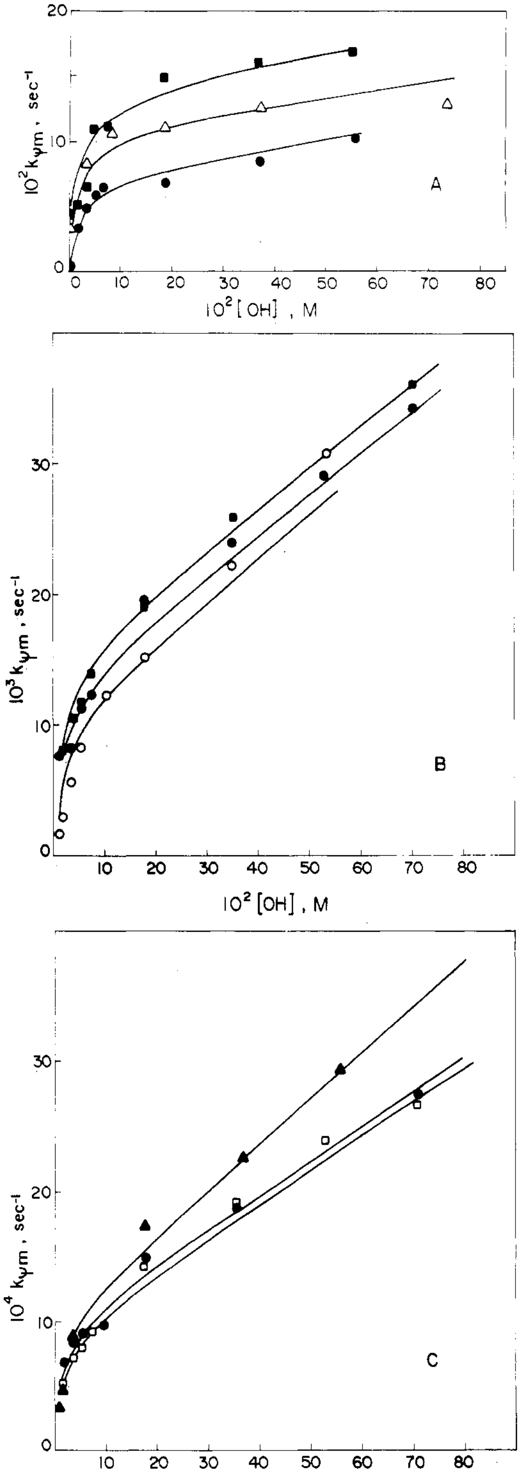

Figure 2. Plot of the observed pseudo-first-order rate constant vs. hydroxide ion concentration at constant added CTAOH. A: DDT, [CTAOH] = 1.46×10^{-3} (●), 3.81×10^{-3} (△), 1.42×10^{-2} (■) M. B: DDD, [CTAOH] = 3.60×10^{-4} (○), 1.46×10^{-3} (●), 7.32×10^{-3} (■) M. C: DDM, [CTAOH] = 8.78×10^{-4} (□), 1.46×10^{-3} (●), and 7.32×10^{-3} (▲) M.

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indicates that the reaction across the interfacial boundary does not depend on the nature of the counterion, an observation which is consistent with our assumption of a phase-transfer catalytic pathway.

We had previously suggested[11] that a micelle-water interface should not be very different from the interface present in systems where phase-transfer catalysis is taking place.

The postulate phase-transfer catalytic term is also reasonable in the light of Aniansson's recent calculations.[23] A dynamic micelle with monomers protruding out of the hydrophobic core will show an effective increase of the micellar surface. This dynamic system, which changes its surface area in a time scale of picoseconds,[23] should facilitate the solubilization and transfer of the pesticides across the Stern layers to the shear surface or interfacial boundary where the phase-transfer catalysis occurs.

Our explanation is in agreement with Bunton and Romsted's original proposal[12] of an additional reaction pathway across the micellar boundary. Even though Bunton, Romsted, and co-workers later on rejected this hyphothesis on the basis of experiments with 2,4-dinitrochloronaphthalene (DNCN) and *p*-nitrophenyl diphenyl phosphate[13] (pNPDPP), our results seem to indicate that their original proposal was correct. In fact, the reported values for $k_{\psi m}$ do increase slightly as a function of NaOH concentration for pNPDPP and remain roughly constant for DNCN. The failure to observe the linear dependence of $k_{\psi m}$ for higher concentrations of base may be probably ascribed to a low value of the rate constant across the boundary combined with a lower range of hydroxide ion concentrations employed as compared to our case.

The observation of the new catalytic term in the reaction under study may also be due to an increase in permeability of the double layer to hydroxide ion since both the increase in hydroxide concentration in solution and the progressive neutralization of the micellar charge, which runs parallel, are factors which decrease the difference in chemical potential between the bulk solvent and the inner part of the double layer. The idea of a fixed number of sites loses then its theoretical meaning under our experimental conditions and the pseudophase separation model no longer applies to our system.

We are currently investigating several reactions at limit conditions, with cationic and anionic detergents, in order to arrive at a more general treatment for micellar catalysis. It is hoped that a model which takes into account processes across the interfacial boundary will be useful for reactions involving many other counterions with a wide range of concentrations.

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Adsorption of NaCl and KCl on Al_2O_3 at 800-900 °C

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Adsorption was observed by measuring the weights of microporous alumina adsorbents as a function of time while they were exposed to varying partial pressures of NaCl and KCl in a stream of Ar. Despite the high experimental temperatures, the results exhibited the characteristics of physical adsorption. Adsorption and desorption were reversible without hysteresis. The kinetics appeared to be limited by transport through the adsorbent pores. The steady-state weight gains were readily described by the BET isotherm. The values of the weight gains at monolayer coverage, deduced from both the steady state and the rate data, were of the size expected from the adsorbent surface areas and estimated molecular cross sections. The phenomenon promises to be useful for removing trace amounts of these corrosive salts from hot combustion gases.

Introduction

Physical adsorption of gases on solids involves physical, van der Waals forces rather than chemical ones.[1,2] Since these are relatively weak in the cases most familiar to us, we are accustomed to thinking of physical adsorption as a phenomenon which occurs only at low temperatures. Indeed, in the vast literature on this subject one can find few references to experiments conducted much above room temperature.[3] However, whenever vapor-phase molecules interact strongly with a solid surface then they ought to be physically adsorbed there even at high temperatures, and that evidently is the situation in the present experiments. Our adsorbates are compact diatomic molecules with very large electric dipole moments, 8.5 and 10.5 D for NaCl and KCl.[4] Electrostatic interactions between these molecules are responsible[5] for the large heats of vaporization of the corresponding salts, 185.9 and 179.3 kJ/mol at 1073 K.[6,7] In a similar way, their electrostatic, purely physical interactions with the surfaces of ionic solids such as Al_2O_3 can lead to uncommonly large physical adsorption energies and, thus, to physical adsorption on these solids at unusually high temperatures.

Physical adsorption at high temperatures has not been much investigated, perhaps, because it has found no practical use heretofore. Recently, however, Lee and Johnson[8] have suggested an application that might have profound technical consequence. They addressed a problem related to the so-called "pressurized fluidized bed combustor/gas turbine" (PFBC/GT) combined cycle system, which is under study as a highly efficient way to use coal for electric power generation.[9] In this system, coal would be burned to produce hot gases (at about 800-950 °C and 10 bar) which, after removal of ash particles, would drive a gas turbine.

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