Acceleration of *o*-Iodosobenzoate-Catalyzed Hydrolysis of *p*-Nitrophenyl Diphenyl Phosphate by Cationic Polymer Colloids

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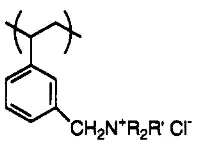
Abstract: Cross-linked polystyrene latexes containing (styrylmethyl)trialkylammonium chloride repeat units greatly accelerate the *o*-iodosobenzoate (IBA) catalyzed hydrolysis of *p*-nitrophenyl diphenyl phosphate (PNPDPP). The half-life of PNPDPP is as short as 3 s with 0.10 mg mL^{-1} of particles containing 24 mol % of (styrylmethyl)tributylammonium chloride repeat units (TBAQ24) and 4×10^{-5} M IBA in TAPS buffer at pH 9.1 and 25.0 °C, and the apparent second-order rate constant (k_{IBA}) exceeds that in the absence of latexes by 6300 times, the largest rate enhancement reported for IBA-catalyzed hydrolysis of PNPDPP in any colloidal or polymeric medium. The k_{IBA} value increases with increasing radius of the quaternary ammonium ion (trimethyl < triethyl < tripropyl < tributyl) and with decreasing mole % of (styrylmethyl)trimethylammonium chloride (TMAQ) repeat units in the latexes. The amounts of IBA and chloride ions bound to latexes were measured directly by UV spectrophotometry and chloride-selective electrode analysis of ultrafiltrates from dispersions, and ion exchange selectivity coefficients for IBA and TAPS anions relative to chloride were calculated. The sizes of water-swollen particles were measured by dynamic and static light scattering. Using an ion-exchange model, the second-order rate constants k_{2L} in the latex phase were estimated from observed rate constants, the percent of IBA bound, and the particle volumes. The 6300 times rate enhancement in the TBAQ24 dispersion is due ten times to a higher intraparticle rate constant and 630 times to higher local concentrations of IBA and PNPDPP in the latex phase. With the most hydrophilic TMAQ latex particles, the rate enhancements are due entirely to higher reactant concentrations in the particles. The intraparticle rate constants at pH 9.1 and the ion exchange selectivity coefficients can be used to predict rate constants as functions of pH, amount of latex particles, and amount of added NaCl.

Association colloids,[1] such as micelles,[1a–k] microemulsions,[1a–d,l,m] and bilayer vesicles,[1a–d,n,o] and polymers, both soluble[2a–e] and insoluble,[2g–l] often enhance rates of chemical reactions in aqueous mixtures. In addition to practical rate enhancements, colloids and polymers provide an opportunity to understand, via controlled experiments, chemical reactivity in heterogeneous aqueous media. Polymeric catalysts are usually designed as heterogeneous analogues of effective homogeneous low molar mass catalysts with the aim of recovery and reuse of the catalyst. Insoluble polymeric catalysts most often have been prepared from cross-linked polystyrene beads that were intended for use as Merrifield resins for solid-phase peptide synthesis or as ion-exchange resins for water treatment. The bead catalysts often are less active than their solution counterparts because rates of reactions are limited by mass transfer of reactants from solution to the bead surface and intraparticle diffusion of reactants from the surface to the active sites within the bead.[2k] The much smaller sizes and greater surface areas per unit mass of colloids than of polymer beads overcome such diffusional limitations.

Polymer colloids, also known as latexes, as catalyst supports combine the advantages of association colloids and insoluble polymers.[3] They are prepared by emulsion polymerization, the method used for production of synthetic rubber, water-based coatings, and adhesives. For study of reactive anions bound to colloids, we have synthesized a family of monodisperse poly(chloromethylstyrene) latexes and converted them to quarternary ammonium ion polymers **1** by reactions with trialkylamines.[4]

1: TMAQ60, R = R' = CH_3
TMAQ39, R = R' = CH_3
TMAQ14, R = R' = CH_3
TEAQ32, R = R' = CH_2CH_3
TPAQ13, R = R' = $CH_2CH_2CH_3$
TBAQ24, R = R' = $CH_2CH_2CH_2CH_3$
HEDMAQ25, R = CH_3, R' = CH_2CH_2OH



The structure **1** named TBAQ24, for example, refers to 24 mol % of tributylamine quaternized repeat units. All of the polymers

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are insoluble due to cross-linking with 1 wt % of divinylbenzene. These latex particles are sub-microscopic anion-exchange resins having varied concentrations and structures of the ion-exchange sites, which control their ability to swell in aqueous dispersions. The 200–300-nm diameters of the latex particles are 50 times larger than the diameters of typical spherical micelles and 200–2000 times smaller than the diameters of typical Merrifield resins and ion-exchange resins. Latex particles can be recovered by ultrafiltration or by coagulation and conventional filtration. The properties of the quaternary ammonium ion latexes are similar to those of both micelles and conventional anion-exchange resins. As colloids they are dispersed in water by Coulombic repulsion, but as cross-linked macromolecules they do not dissociate and reassociate in dynamic equilibrium, as the surfactant molecules of micelles do.

We are systematically studying reactions having different kinetic orders, and reactive species of different charge types, to understand how the latexes affect rates of heterogeneous reactions. The catalytic effects of latexes may be due to high concentrations of absorbed reactants in the particle phase, to greater rate constants in the particle phase than in water, or to both. For example, the observed rate constants of the unimolecular decarboxylation of 6-nitrobenzisoxazole-3-carboxylate are 220 and 10 500 times greater in TMAQ60 (for trimethylamine quaternized repeat units) and TBAQ24 dispersions than in water, and the intraparticle rate constants are 310 and 21 000 times greater at ambient temperature.[4a] The higher activity of TBAQ24 than of TMAQ60 is due to a less hydrophilic environment in the TBAQ24 particles.

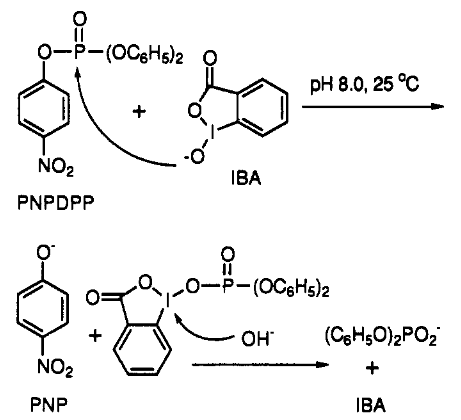
In this paper we describe the first complete analysis of the rates of a bimolecular reaction in a polymer latex. The kinetic model is similar to those applied to other colloids and polymers in aqueous media, such as micelles,[1e–k] microemulsions,[1l,m] vesicles,[1n,o] and soluble polyelectrolytes.[2b–f] We assume no mass transfer or intraparticle diffusional limitations to the rates of reaction. In all of these media the overall rates of bimolecular nucleophilic reactions are the sums of the rates of reaction in the aqueous phase (w) and in the particle phase (p), as shown in eq 1. The overall rates depend upon the second-order rate constants

$$\text{rate} = k_{2w}[S]_w[N]_w + k_{2p}[S]_p[N]_p \qquad (1)$$

k_{2w} and k_{2p} and upon the equilibrium constants for partitioning of the nucleophile (N) and the substrate (S) between the two phases. The particle phases range from large polymer beads, such as ion-exchange resins, to "pseudophases" such as surfactant micelles and soluble polyelectrolytes. The equilibrium constants may be called ion exchange selectivity coefficients, as in this paper, partition coefficients, as in the liquid–liquid extractions of phase-transfer catalysis, or binding constants, as in micellar and polyelectrolyte solutions in which kinetics are usually modeled by an enzyme-like mechanism. In all cases the equilibrium concentrations of lipophilic organic substrates are much higher in the particle phase than in water. The equilibrium concentration of a nucleophilic anion in the particle phase is higher than in water due to both Coulombic and van der Waals forces. Cationic micelles and polyelectrolytes accelerate the rates of these bimolecular reactions due to high concentrations of the nucleophile in the particle phase, whereas anionic micelles and polyelectrolytes retard the rates by binding the substrate and excluding the nucleophile. The rate constants of nucleophilic reaction in the two phases depend mainly on the activity of the nucleophile, which is generally higher in organic media than in water, where the ground state of the nucleophile is stabilized by hydrogen bonding. When the particle phase is highly aqueous, such as the surface of a micelle or a polyelectrolyte, the activity of the nucleophile is usually not much different from its activity in water.

Here we report the kinetics of hydrolysis of *p*-nitrophenyl diphenyl phosphate (PNPDPP) catalyzed by *o*-iodosobenzoate ion (IBA) in the presence of quaternary ammonium ion latexes **1**. (IBA is an acronym for *o*-iodosobenzoic acid, and we use IBA to designate the catalytically active anion, which exists in the cyclic form shown in Scheme 1). The hydrolysis of PNPDPP is a prototype for the hydrolysis of organophosphorus insecticides and chemical warfare agents.[5] IBA shows spectacular catalytic activity in micelles[6,7] and high activity also in microemulsions[8] and other colloidal and polymeric media.[9] The polymer latexes[10] TMAQ17 and TMAQ34 and CTACl (cetyltrimethylammonium chloride) micelles[6a] give half-lives of hydrolysis of about 10 s at 25 °C with IBA concentrations of $\leq 10^{-4}$ M and ≤ 1 mg mL^{-1} of dispersed particles and surfactants and are by far the most active media reported for this reaction. The reaction mechanism is shown in Scheme 1.[6] In latexes the kinetics are first-order in PNPDPP and first-order in IBA and have only a small dependence on pH (at pH > 8), indicating that attack of the IBA on phosphorus is rate-limiting. We have reported many aspects of the kinetics with a more limited group of latexes.[10] However, in the previous investigation we did not evaluate the binding constants for binding of the IBA to the particles and the intraparticle rate constants. Analysis of the second-order kinetics must account for the partial dissociation of two weak acids, *o*-iodosobenzoic acid and the buffer (TAPS, *N*-(tris[hydroxymethyl]methyl)-3-aminopropanesulfonic acid), which partition between the particle phase and the aqueous phase. We have now measured ion exchange selectivity coefficients of IBA, TAPS anion, and chloride ion in the latexes and calculated the intraparticle second-order rate constants from the observed rate constants, the selectivity coefficients, and the volumes of the swollen latex particles.

Scheme 1



Results

Particles. The latexes **1** were prepared by shot growth emulsion copolymerizations[11] of varied proportions of styrene and

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Table 1. Latex Compositions and Sizes

latex	N^+/g[a]	density, g mL^{-1} [b]	d_w, nm[c]	d_h, nm[d]	V, M^{-1} [e]
TBAQ24	1.60	1.079	162	224	1.53
TPAQ13	0.92	1.062	151	200	2.38
TEAQ32	2.13	1.092	155	280	2.53
TMAQ14	1.15	1.064	166	206	1.56
TMAQ39	2.63	1.104	147	256	0.85[f]
HEDMAQ25	1.66	1.080	151	236	2.13
TMAQ60	3.41	1.142	177	342	0.86[f]

[a] mequiv of N^+ per gram of dry latex. [b] Reference 4. [c] Weight average diameter from TEM.[4] [d] Hydrodynamic diameter from dynamic light scattering at pH 9.10, 5 mM TAPS. [e] Volume per mole of quaternary ammonium ions in the latex phase. $V = (d_h^3/d_w^3)/(g/mL)(N^+/g)$. [f] The diameter of gyration d_g was used.[16] d_g = 198 nm for TMAQ39; d_g = 265 for TMAQ60. See structure **1** for definitions of latexes.

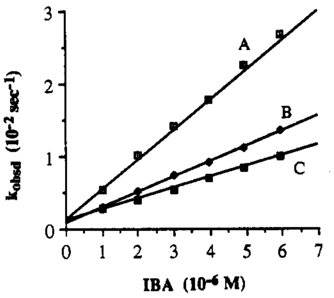

Figure 1. Dependence of k_{obsd} on IBA concentration in 0.1 mg mL^{-1} latex dispersions in pH 8.00, 5.0 mM TAPS, with 1.99 × 10^{-5} M PNPDPP: (A) TBAQ24; (B) TEAQ32; (C) HEDMAQ25.

(chloromethyl)styrene with 1.0 wt % of divinylbenzene as a cross-linker and 1.0 wt % of (styrylmethyl)trimethylammonium chloride to provide surface charge stabilization during polymerization.[4] All additional quaternary ammonium groups were created by reactions of the preformed latexes with tertiary amines. After synthesis the latexes were washed and ultrafiltered extensively to remove residual salts, monomers, and polyelectrolytes. The latex properties are reported in Table 1. The particle sizes were measured in dry form by transmission electron microscopy (TEM) and in aqueous dispersions by dynamic light scattering (DLS). The larger diameters of wet than of dry latexes indicate substantial swelling.

Kinetics. Rates of hydrolysis of PNPDPP at 25.0 °C were measured by the appearance of the UV absorbance of *p*-nitrophenoxide ion in latex dispersions. Despite some light scattering, standard absorbance measurements were possible because so little of the latexes was required to effect catalysis. For example, the turbidity ($\log[I_0/I]$) of 0.2 mg mL^{-1} of TBAQ24 latex at 400 nm is 0.94. In an early experiment with 0.10 mg mL^{-1} of TBAQ24 and 4 × 10^{-5} M IBA at pH 8.0, the PNPDPP (2 × 10^{-5} M) had a half-life of 3 s. For conveniently slower rates of hydrolysis all other experiments with latexes were carried out with IBA ≤ 5.9 × 10^{-6} M. Good pseudo-first-order kinetics were obtained for at least 3 half-lives. For each amount and type of latex studied, rate constants (k_{obsd}) for pseudo-first-order hydrolysis of PNPDPP were measured at five or six IBA concentrations in 5.0 mM TAPS buffer solutions at pH 8.0 and 9.1. The plots of k_{obsd} vs $[IBA]_t$ (total concentration of IBA) are linear, as shown in Figures 1 and 2. From the rate equation (2) the

$$d[PNP]/dt = k_{obsd}[PNPDPP] = (k_0 + k_{IBA}[IBA]_t)[PNPDPP] \quad (2)$$

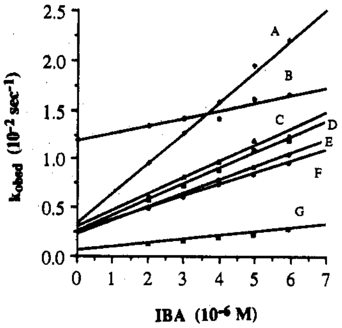

Figure 2. Dependence of k_{obsd} on IBA concentration in 0.2 mg mL^{-1} latex dispersions in pH 9.10, 5.0 mM TAPS, with 1.99 × 10^{-5} M PNPDPP: (A) TBAQ24; (B) HEDMAQ25; (C) TPAQ13; (D) TEAQ32; (E) TMAQ14; (F) TMAQ39; (G) TMAQ60.

Table 2. k_{IBA} at pH 8.00 with 0.10 mg of Latex per mL[a]

latex	$[N^+]$, mM[b]	k_{IBA}, M^{-1} s^{-1}
TBAQ24	0.160	4300
TEAQ32	0.213	2120
HEDMAQ25	0.166	1480
TMAQ17[c]	0.548	1722
TMAQ34[d]	0.968	1359

[a] TAPS buffer, 5.0 mM, at 25.0 ± 0.1 °C. Estimated error limits in k_{IBA} are ±30 M^{-1} s^{-1}. [b] mmol of $[N^+]$ groups per liter of dispersion. [c] Reference 10; 0.4 mg mL^{-1} of TMAQ17 latex; 1.37 mmol N^+ g^{-1}; V = 1.49 M^{-1}. [d] Reference 10; 0.4 mg mL^{-1} of TMAQ34 latex; 2.43 mmol N^+ g^{-1}; V = 0.72 M^{-1}.

Table 3. Rate Constants at pH 9.10 with 0.20 mg of Latex per mL[a]

latex	N^+, mM[b]	k_{IBA}, M^{-1} s^{-1}	k_0 (10^{-3} s^{-1})[c]	k_{2L}, M^{-1} s^{-1} [d]
TBAQ24	0.321	3190	3.30	5.5
TPAQ13	0.180	1700	2.95	2.6
TEAQ32	0.427	1630	2.45	5.7
TMAQ14	0.230	1410	2.18	3.7
TMAQ39	0.526	1200	2.50	1.8
HEDMAQ25	0.332	770	11.9[e]	2.2
TMAQ60	0.682	370	0.554	0.57
none		0.51[f]	0.0227	

[a] TAPS buffer, 5.0 mM, at 25.0 ± 0.1 °C. [b] Concentration of quarternary ammonium units of dispersion. [c] Calculated by extrapolating the data in Figure 2 to k_{obsd} in the absence of IBA according to eq 2. [d] The second-order catalytic rate constant in the latex phase. The standard deviation is 0.3 M^{-1} s^{-1}. [e] Experimental k_{obsd} = 12.0 × 10^{-3} s^{-1} in the absence of IBA. [f] k_{2w} of Scheme 2.

intercepts are the pseudo-first-order rate constants, k_0, of hydrolysis in the absence of IBA and the presence of particles, and the slopes are the second-order catalytic rate constants, k_{IBA}. In the absence of latex particles, the rate constants for pseudo-first-order hydrolysis of PNPDPP at pH 9.10 were measured using excess IBA. The results are reported in Tables 2 and 3.

Binding of IBA to Particles. The amount of IBA bound to each latex in 5 mM TAPS at pH 9.1 was determined by UV spectrophotometric analysis of the IBA in the ultrafiltrate from a 0.1 mg mL^{-1} latex dispersion. Since the pK_a of the conjugate acid of IBA is 7.02,[8a] >99% of the IBA in the aqueous phase is in anionic form at pH 9.10. The data were analyzed by the mechanism of Scheme 2. The subscripts w and L refer to the water and latex phases. The fraction of IBA bound to latex is reported in Table 4.

Intraparticle Rate Constants. An ion-exchange model, similar to the pseudo-phase ion exchange model of micellar catalysis,[1e-k] was used to calculate the second-order rate constants k_{2L} in the latex phase. The model, shown in Scheme 2, depends on three approximations: (1) Exchange of IBA, chloride, and buffer ions is much faster than chemical reaction. This is reasonable even for a reaction with a 3-s half-life, since the time for 50% exchange of an isotopic tracer ion by diffusion in a spherical particle is given by

$$t_{1/2} = 0.030 r_0^2/D \quad (3)$$

where r_0 is the radius of the sphere and D is the self-diffusion

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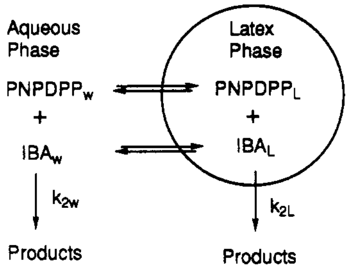
Scheme 2



Ion Exchange Model

Table 4. Anion Exchange Selectivity Coefficients of Latexes[a]

latex	IBA_b/IBA_t[b]	$K_{IBA/TAPS}$[c]	$K_{TAPS/Cl}$[d]	$K_{IBA/Cl}$
TBAQ24	0.144	6.2	0.27	1.7
TPAQ13	0.139	(10)	(0.3)	(3)
TEAQ32	0.154	(5)	(0.3)	(1.5)
TMAQ14	0.069	(3.3)	(0.3)	(1.0)
TMAQ39	0.145	3.9	0.37	1.4
HEDMAQ25	0.124	*e*	*e*	*e*
TMAQ60	0.190	4.2	0.58	2.4

[a] pH 9.10 TAPS buffer, 5.0 mM, at 25 °C. [b] Fraction of IBA bound when $[IBA]_t \ll [Cl]_t < [TAPS]_t$ with 0.1 mg mL^{-1} of latex and 5 mM $[TAPS]_t$. Estimated error limits are ±0.02. [c] See eq 6. [d] See eq 8. Values in parentheses assume $K_{TAPS/Cl} = 0.3$. [e] Not determined.

coefficient of the ion.[12] Since diffusion coefficients of univalent counterions in quaternary ammonium ion resins are typically 10^{-7} to 10^{-5} cm^2 s^{-1}, the times required for 50% exchange are on the order of 1–100 μs. (2) The sum of concentrations of bound anions equals the concentration of quaternary ammonium ions. This electroneutrality approximation is valid for ion-exchange resins.[13] Although degrees of dissociation of counterions from quaternary ammonium ion latexes have not been reported, the degrees of dissociation of protons and of sodium ions from latexes having arenesulfonic acid groups on the surface decrease as the number of functional groups per particle increases.[14] Since the number of ionic groups in every one of our latex samples exceeds that of a sulfonic acid latex having a degree of dissociation of 0.04,[14] the electroneutrality approximation is valid for calculation of concentrations of counterions. (3) PNPDPP is 100% bound to particles. This approximation may overestimate the amount of PNPDPP bound and therefore underestimate the intraparticle rate constants. We discuss this point later.

For calculation of the intraparticle second-order rate constants, we use V, the particle volume per mole of quaternary ammonium ions. The volume of each type of particles was calculated from the hydrodynamic diameter d_h determined by dynamic light scattering (Table 1), except for TMAQ39 and TMAQ60, for which the radius of gyration determined from the angular dependence of static light scattering was used because of anomalously large experimental values of d_h.[15] For a sphere of uniform density of polymer chain segments $d_g = 0.775d_h$. Since the fraction of IBA bound to the latex and the molar volume V of latex particles (Table 1) are determined independently, the concentration of IBA in the latex phase can be calculated using eq 4, which converts moles of IBA bound to particles per liter of dispersion, $[IBA]_b$, to moles of IBA bound per liter of particles, $[IBA]_L$. $[N^+]$ is the molar concentration of latex quaternary ammonium ions in the dispersion. The second-order rate constants, k_{2L}, in the particle phase are calculated as the least squares slopes of the plots of k_{obsd} vs $[IBA]_L$ according to eq 5 and are reported in Table 3.

$$[IBA]_L = [IBA]_b/[N^+]V \qquad (4)$$

$$d[PNP]/dt = k_{obsd}[PNPDPP] = (k_0 + k_{2L}[IBA]_L)[PNPDPP] \qquad (5)$$

Ion-Exchange Selectivity. IBA, Cl, and TAPS buffer anions compete for the quaternary ammonium ion-exchange sites. The equilibria are described by three selectivity coefficients (eqs 6–8)

$$K_{IBA/TAPS} = [IBA]_b[TAPS]_f/[IBA]_f[TAPS]_b \qquad (6)$$

$$K_{IBA/Cl} = [IBA]_b[Cl]_f/[IBA]_f[Cl]_b \qquad (7)$$

$$K_{TAPS/Cl} = [TAPS]_b[Cl]_f/[TAPS]_f[Cl]_b \qquad (8)$$

in which the subscripts b and f refer to bound and free ions and all concentrations are based on the total volume of dispersion. Determination of any two of the three selectivity coefficients also determines the third, since $K_{IBA/TAPS} = K_{IBA/Cl}/K_{TAPS/Cl}$. Values of $K_{TAPS/Cl}$ were determined for three latexes in the absence of IBA by analysis of $[Cl]_f$ in ultrafiltrates of latex dispersions in 5 mM TAPS at pH 9.1. From the experimental values of $[IBA]_b/[IBA]_t$ (Table 4) and $K_{TAPS/Cl}$, the other selectivity coefficients were calculated as follows. Equation 6 requires values of $[TAPS]_b$ and $[TAPS]_f$, which we calculate using three approximations: (1) None of the zwitterionic form of TAPS is bound to particles. This is reasonable because the volume percent particles in the dispersion is less than 0.1% and the TAPS zwitterion is hydrophilic. Even the TAPS anion is not strongly bound. (2) The concentration of TAPS anion in the aqueous phase is $[TAPS]_f = (0.84)([TAPS]_t - [TAPS]_b)$. In water TAPS has p$K_a$ 8.4 and is 84% ionized at pH 9.1. The subscript t refers to the total amount of TAPS in acid and base forms. (3) $[TAPS]_b + [Cl]_b = [N^+]$, since under all of the experimental conditions $[IBA]_t = 2 \times 10^{-5}$ M, $[TAPS]_t = 5 \times 10^{-3}$ M, $[Cl]_t = (1.80\text{–}6.82) \times 10^{-4}$ M, $[IBA]_b$ is small with respect to $[TAPS]_b$ and $[Cl]_b$, and we assume a negligible fraction of counterions dissociated from the particle. These conditions lead to quadratic eq 9, which was used to calculate $[TAPS]_b$.

$$(1 - x)[TAPS]_b^2 + x([TAPS]_t + [N^+])[TAPS]_b - x[TAPS]_t[N^+] = 0 \qquad (9)$$

where $x = 0.84K_{TAPS/Cl}$. $[TAPS]_b$ and approximation 2 give $[TAPS]_f$. The values of $[TAPS]_b$ and $[TAPS]_f$ and the experimental $[IBA]_b/[IBA]_t$ data give $K_{IBA/TAPS}$ from eq 6.

We measured $K_{TAPS/Cl}$ for the TBAQ24, TMAQ39, and TMAQ60 latexes, for which the most kinetic data were obtained. The selectivity coefficients are in Table 4. Since the other latexes were less hydrophilic than TMAQ39, we assumed they have $K_{TAPS/Cl} = 0.3$ to estimate their $K_{IBA/TAPS}$ values.

Calculation of Rate Constants at pH 8.0. To compare the new results of this investigation with earlier kinetic data for IBA-catalyzed PNPDPP hydrolysis in latexes, we used the intraparticle rate constants k_{2L} at pH 9.1 from Table 3 and the ion-exchange selectivity coefficients from Table 4 to estimate rate constants at pH 8.0. For these calculations we assume that the k_{2L}, the selectivity coefficients, and the molar volumes of particles, V, are

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(12) Helfferich, F. *Ion Exchange*; McGraw-Hill: New York, 1962; pp 261–262.

(13) Helfferich, F. *Ion Exchange*; McGraw-Hill: New York, 1962; pp 133–136.

(14) Ito, K.; Ise, N.; Okubo, T. *J. Chem. Phys.* **1985**, *82*, 5732.

(15) The hydrodynamic diameters d_h of the TMAQ60 and TMAQ39 particles, which were calculated from the diffusion coefficients by the Stokes–Einstein equation

$$d_h = k_B T/3\pi\eta D$$

where k_B is the Boltzmann constant, η is the coefficient of viscosity of the solvent, and D is the self-diffusion coefficient, are markedly reduced by the electroviscous effect of a large counterion shell around the swollen, charged particles.[16] Thus d_g is better than d_h for measurement of the volume of the water-swollen particles.

(16) Davis, K. A.; Ackerson, B. J.; Yu, H.; Ford, W. T.; Xia, J.; Dubin, P. L. *Langmuir*. Submitted for publication.

Table 5. Calculated vs Experimental k_{IBA} at pH 8.0[a]

latex	concn, mg mL^{-1}	k_{IBA}, M^{-1} s^{-1} calcd	k_{IBA}, M^{-1} s^{-1} exptl
TBAQ24	0.10	7400	4300
TEAQ32	0.10	3500	2120
TMAQ17	0.40	1760	1720[b]
TMAQ34	0.40	1200	1360[b]
TMAQ60	0.40	230	540[b]

[a] 5 mM TAPS buffer, 25.0 °C. [b] Reference 10.

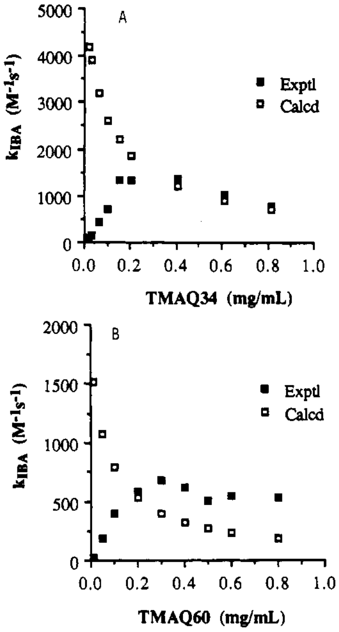

Figure 3. Calculated and experimental k_{IBA} at 25 °C in 5 mM TAPS buffer at pH 8.0 as a function of amount of particles in the dispersion: (A, top) TMAQ34; (B, bottom) TMAQ60.

independent of pH. From the TAPS buffer pK_a = 8.4 and the approximation that none of the zwitterionic form of TAPS is in particles, at pH 8.0 $[\mathrm{TAPS}]_f = 0.29([\mathrm{TAPS}]_t - [\mathrm{TAPS}]_b)$. Similarly from the *o*-iodosobenzoic acid pK_a = 7.02 and the approximation that none of the acid form of IBA is in particles, at pH 8.0 $[\mathrm{IBA}]_f = 0.90\ ([\mathrm{IBA}]_t - [\mathrm{IBA}]_b)$. These approximations, the selectivity coefficient equations (eqs 6–8), and mass balances give quadratic eq 10, where $x = 0.29K_{\mathrm{TAPS/Cl}}$.

$$(1-x)[\mathrm{Cl}]_b^2 - \{[\mathrm{N}^+] + [\mathrm{Cl}]_t + x([\mathrm{TAPS}]_t - [\mathrm{N}^+])\}[\mathrm{Cl}]_b + [\mathrm{N}^+][\mathrm{Cl}]_t = 0 \quad (10)$$

The values of $[\mathrm{Cl}]_b$ from eq 10, $[\mathrm{Cl}]_f$ from mass balance, and $K_{\mathrm{IBA/Cl}}$ are used to calculate $[\mathrm{IBA}]_b$ from eq 7. Equations 2, 4, and 5 give eq 11 for calculation of k_{IBA} at pH 8.0.

$$k_{\mathrm{IBA}} = ([\mathrm{IBA}]_b/[\mathrm{IBA}]_t)(k_{2\mathrm{L}}/[\mathrm{N}^+]V) \quad (11)$$

Results of these estimates of k_{IBA} at pH 8.0 for five latexes are in Table 5, and comparisons with experimental data[10] over wide ranges of particle concentrations for TMAQ34 and TMAQ60 particles are in Figure 3.

Added NaCl depresses the rates of IBA-catalyzed hydrolysis of PNPDPP in latex dispersions because the chloride ion competes with IBA for ion-exchange sites in the latex. Application of eqs 2, 10, and 11, and the additional approximations that the intraparticle rate constant $k_{2\mathrm{L}}$ and the molar volume of the particles V are independent of NaCl concentration, gave calculated values of the pseudo-first-order rate constants k_{obsd} for TMAQ34 and TMAQ60 dispersions. The results are compared with experimental data[10] in Figure 4. The only difference in application of eq 10 without and with added NaCl is that in the latter case the mass balance of chloride ion is $[\mathrm{Cl}]_t = [\mathrm{NaCl}] + [\mathrm{N}^+]$.

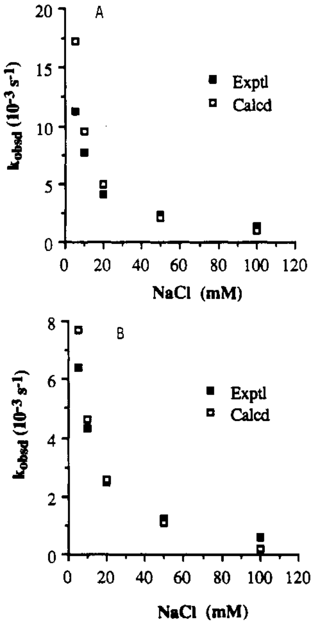

Figure 4. Calculated and experimental k_{obsd} at 25 °C in 5 mM TAPS buffer at pH 8.0 as a function of concentration of added NaCl: (A, top) 0.2 mg mL^{-1} TMAQ34; (B, bottom) 0.2 mg mL^{-1} TMAQ60.

Discussion

The hydrated latex particles used here have diameters of 200–300 nm, 50 times larger than typical micelles and 2000 times smaller than typical ion-exchange resin beads. Pseudo-first-order kinetics to high conversion prove that neither mass transfer nor diffusion of IBA or PNPDPP to the active sites limits the rate of reaction in any of the particle dispersions. Thus the mechanism of reaction is the same as that in aqueous solution, rate-limiting attack of IBA on the PNPDPP followed by rapid conversion of the IBA–phosphate adduct to IBA and diphenyl phosphate ion as shown in Scheme 1.[6]

In contrast, when large ion-exchange resin beads are used for the IBA-catalyzed hydrolysis of PNPDPP, two-stage kinetics are observed: first a "burst" of *p*-nitrophenoxide ion is detected, and then the remaining PNPDPP hydrolyzes more slowly.[9ab] This is a consequence of rapid reaction of the IBA and PNPDPP initially bound to the resin, followed by slow mass transfer and/or intraparticle diffusion of the remaining PNPDPP. There usually are mass transfer and diffusional limitations to the rates of fast polymer-supported phase-transfer-catalyzed reactions.[2k]

The second-order rate constants, k_{IBA} (Table 3) at pH 9.1, are 700–6300 times faster with 0.2 mg mL^{-1} of latex than without latex. Although k_{IBA} values decrease with decreasing ionic radius of the quaternary ammonium ions, butyl > propyl > ethyl > methyl, the intraparticle rate constants $k_{2\mathrm{L}}$ for the varied alkyl groups cannot be compared well because of wide variation of the quaternary ammonium ion contents of the particles. Among the TMAQ ([styrylmethyl]trimethylammonium) ion latexes, k_{IBA} and $k_{2\mathrm{L}}$ values decrease with increasing concentration of ionic groups and increasing water content in the particles: TMAQ14 > TMAQ39 > TMAQ60.

These latexes show the same order of activities for decarboxylation of 6-nitrobenzisoxazole-3-carboxylate[4a] as for hydrolysis of PNPDPP. The rates of decarboxylation in protic media depend mainly on ground-state stabilization due to hydrogen bonding.[17] Although intraparticle decarboxylation rate constants were determined for only three of the latexes, they follow the same trend as the intraparticle second-order rate constants $k_{2\mathrm{L}}$ for IBA-catalyzed hydrolysis of PNPDPP. Thus the IBA

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(17) (a) Kemp, D. S.; Paul, K. G. *J. Am. Chem. Soc.* **1975**, *97*, 7305. (b) Kemp, D. S.; Cox, D. D.; Paul, K. G. *J. Am. Chem. Soc.* **1975**, *97*, 7312. (c) Grate, J. W.; McGill, R. A.; Hilvert, D. *J. Am. Chem. Soc.* **1993**, *115*, 8577.

Table 6. k_{IBA} in TBAQ24 Latex vs Micelles

colloid	k_{IBA}, $\mathrm{M^{-1}\,s^{-1}}$	pH	buffer/electrolyte
latex	4300	8.0	0.005 M TAPS
$H(CH_2)_{16}N^+(CH_3)_3Cl^-$ [a]	645	8.0	0.02 M NaH_2PO_4/Na_2HPO_4 μ = 0.08 M NaCl
latex	3190	9.1	0.005 M TAPS
$H(CH_2)_{16}N^+(CH_3)_3Br^-$ [b]	1900	9.2	0.01 M $Na_2B_4O_7$/HCl

[a] Reference 6b. [b] Reference 18a.

reactivities in the latexes decrease as stabilization of IBA by hydrogen bonding increases.

The mechanism of action of the latex HEDMAQ25 (25 mol % of (2-hydroxyethyl)dimethylamine quaternized repeat units) is a special case. At pH 9.1 it is more than 4 times as active as any other latex in the absence of IBA, as shown in Figure 2 and as k_0 in Table 3. We attribute that activity to nucleophilic catalysis by the zwitterion **2**. At pH 8.0 there is much less **2** present, and the activity of HEDMAQ25 in the absence of IBA is not different from that of the other latexes (Figure 1). In the absence of IBA all of the other latexes give k_{obsd} 24–145 times greater than in the absence of particles.

$$ArCH_2N^+(CH_3)_2CH_2CH_2O^-$$

2

There are striking similarities between micellar catalysis and latex catalysis of the reaction of IBA with PNPDPP. Of all heterogeneous media studied, only latexes and CTACl micelles above the critical micelle concentration (0.32 mg mL^{-1}) give half-lives of 10 s or less. In micelles the rate using a more lipophilic octyloxy IBA derivative is 100 times faster than the rate using unsubstituted IBA.[6b] With the most lipophilic latex, TBAQ24, 4×10^{-5} M IBA (less than in the micelle experiments) and 0.1 mg mL^{-1} of particles gave a half-life of 3 s, the shortest we could measure. Comparisons of the most active latex, TBAQ24, with micelles are in Table 6.

We have calculated intraparticle second-order rate constants k_{2L} using the ion-exchange model of Scheme 2, which is similar to the pseudo-phase ion exchange (PIE) model of micellar catalysis.[1e–k] The PIE model fits data to five parameters, which we compare here with latex catalysis: (1) The fraction of surfactant in micellar aggregates. A critical micelle concentration of free surfactant molecules in solution is in equilibrium with micellar aggregates. However, there is no polymer dissociated from a cross-linked latex particle, so this parameter need not be considered. (2) The fraction of counterions bound to the micelle. The 200–300-nm latex particles are about 50 times larger than spherical micelles and have 50 times smaller surface to volume ratio. Most of the ionic groups of these latexes are inside, not on the surface. The fraction of counterions dissociated from micelles is large,[1f] but the fraction dissociated from conventional ion-exchange resins is too small to measure except by electrophoresis.[13] Since only 4% of protons are dissociated from polystyrenesulfonic acid latex particles having fewer ionic groups than the particles in this research,[14] we approximated no dissociation of counterions. (3) The fraction of reactive anions bound. We measured directly the fraction of IBA bound at pH 9.1. In most cases of micellar catalysis this quantity cannot be measured. (4) The fraction of substrate bound. We assumed that all substrate was bound to the latex, incorrectly in some cases, as discussed in the next paragraph. (5) The second-order rate constant in the micellar phase. This requires estimation of the volume of the reactive phase, which in micellar catalysis is that of the Stern layer. The volumes of the latex particles are measured by dynamic and static light scattering. In most cases of micellar catalysis, the fractions of reactive anion and substrate bound and the intramicellar second-order rate constant must be determined by regression analysis of kinetic data. Our treatment of latex catalysis provides estimates of the intraparticle rate constant from experimental rate data, particle volumes, and amounts of IBA bound.

Previously we equilibrated PNPDPP with 0.02 mg mL^{-1} of TMAQ particles, ultrafiltered the dispersions, measured the amounts of PNPDPP in the filtrate, and measured the amounts of PNPDPP recovered from the micropore filter by washing with acetonitrile.[10] No PNPDPP and an amount of the reaction product *p*-nitrophenoxide ion due to 5% hydrolysis were found in the ultrafiltrate, and ≥80% of the PNPDPP was found in the retentate. We concluded that all of the PNPDPP was bound to the particles, within limits of experimental error, at particle concentrations ≥0.02 mg mL^{-1}. Figure 3 shows experimental data[10] and rate constants corresponding with those same experiments calculated from the pH 9.1 intraparticle rate constants k_{2L}, the particle volumes, and the ion-exchange selectivity coefficients reported in the Results. The assumption that all PNPDPP is bound to particles at all particle concentrations leads to decreasing k_{IBA} over the entire range of particle concentrations. That assumption is valid only for particle concentrations >0.2 mg mL^{-1}, according to the comparisons in Figure 3. The increasing experimental values of k_{IBA} up to 0.2–0.3 mg mL^{-1} of particles must be due to increasing amounts of PNPDPP bound. The decreasing experimental values of k_{IBA} at >0.2–0.3 mg mL^{-1} of particles agree with the values calculated from the ion-exchange model, indicating that at those higher particle concentrations the assumption that all PNPDPP is bound is reasonable. The calculated k_{IBA} values in Figure 3 depend on the assumption that all PNPDPP is bound to 0.2 mg mL^{-1} of particles at pH 9.1, the conditions of experiments used to calculate intraparticle rate constants k_{2L}. Therefore the k_{2L} values in Table 3 are lower limits to the true values. If less than 100% of PNPDPP was bound in the pH 9.1 experiments, the actual values of k_{IBA} at pH 8.0 in Figure 3 are larger.

What went wrong with the previous experiments in which no PNPDPP was detected in the ultrafiltrates? We suspect that the solubility of PNPDPP in water is indeed indetectably low (by UV) and that droplets or microcrystals of PNPDPP were retained by the ultrafiltration membrane along with the particles.

In Table 5 and Figure 3 there is good agreement of experimental and calculated k_{IBA} values at pH 8.0 for 0.40 mg mL^{-1} of TMAQ17 and TMAQ34. The poorer agreement for 0.10 mg mL^{-1} of TBAQ24 and TEAQ32 (32 mol % of triethylamine quaternized repeat units) is probably due to incomplete binding of PNPDPP. We do not have an explanation for the differences of about a factor of 2 between calculated and experimental data for TMAQ60.

Figure 4 shows the calculated and experimental effects of adding electrolyte to the reaction mixture. Added chloride ion depresses the rate of hydrolysis by displacing IBA from the latex. In view of all of the approximations in the calculations, the agreement with experimental rate constants is excellent.

The lower limit of the intraparticle rate constant k_{2L} is about the same as the second-order rate constant in water for the most hydrophilic latex TMAQ60 and 10 times larger than that in water for the most lipophilic latex TBAQ24. The CTABr micellar k_{2L} (Table 3) is about twice that in water.[18] Therefore the 6300-fold accelerated rate of hydrolysis of PNPDPP with TBAQ24 is due to both higher intraparticle concentrations of the reactants and higher k_{2L}, and the 700-fold acceleration with TMAQ60 is due mainly to higher intraparticle concentrations of IBA and PNPDPP.

The rate-enhancing effects of the latexes are due in part to the selectivity of the ion-exchange particles for IBA. Normally polystyrene-based anion-exchange resins bind organic anions more

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(18) (a) Leslie, D. R. *Aust. J. Chem.* **1989**, *42*, 2119. (b) Leslie, D. R.; Pantelidis, S. *Aust. J. Chem.* **1990**, *43*, 937.

strongly than chloride ion,[19] so selectivity for IBA over chloride is expected. However, the selectivity coefficients $K_{TAPS/Cl} = 0.27$–0.58 are surprising. The TAPS anion (**3**) binds to the latex less well than chloride ion.

$$(HOCH_2)_3CCH_2NH(CH_2)_3SO_3^-$$

3

The activities of latex dispersions as catalytic media vary with the composition and concentration of the buffer and other electrolytes in the dispersion. Our use of 5 mM TAPS buffer was based on considerations of colloidal stability. At much higher TAPS concentrations, such as 0.1 M, some of the latexes slowly coagulate, which increases light scattering and interferes with spectrophotometric measurements of reaction rates. An NaCl concentration of 1.0 M and phosphate buffers also cause slow coagulation. With mild agitation the coagulation can often be prevented. However, higher concentrations of anions that compete with IBA for binding sites will decrease the rates of reaction of IBA in latex dispersions, as shown in Figure 4. If IBA is to be effective in the decontamination of toxic organophosphates in colloidal media, it should be tested at higher concentrations of buffers, electrolytes, particles, and substrates.

Conclusions

The kinetics of bimolecular nucleophilic reactions in quaternary ammonium ion latex dispersions can be modeled by the same methods used for association colloids, which describe overall rates of reaction in terms of rate constants in the aqueous and particle phases and equilibrium distributions of reactants between the two phases. Unlike the kinetics of polymer-supported phase-transfer catalysis, where slow intraparticle diffusion in >20-μm diameter particles may affect overall rates of reaction even when half-lives of pseudo-first-order reactions are tens of minutes,[2k] the assumption of equilibrium distribution of reactants is valid in 0.2-μm diameter latex dispersions.

As in most micelle-enhanced bimolecular nucleophilic reactions,[1e–k] the intraparticle second-order rate constants are within a factor of 10 of the rate constants in water. The overall rate constants increase markedly with increasing radius of the quaternary ammonium ions (methyl < ethyl < propyl < butyl), due to favorable equilibrium and intraparticle kinetic effects, just as in liquid–liquid phase-transfer catalysis[20] and polymer-supported phase-transfer catalysis.[2k] The tributylammonium ion latexes are expected to enhance greatly the rates of many other bimolecular reactions of water-soluble nucleophilic anions with organic substrates, as long as high concentrations of electrolytes do not cause coagulation of the charged colloidal particles.

Experimental Section

The latexes,[4] chemicals,[10] and kinetic methods[10] are reported elsewhere. Kinetic runs at 25.0 ± 0.1 °C were followed by the appearance of UV absorbance of the hydrolysis product *p*-nitrophenoxide ion (PNP) using a Hewlett-Packard 8452A diode array spectrophotometer. A red shift in the absorption maximum of PNP was found in the latex dispersions. The λ_{max} of PNP, depending on the lipophilicity of latexes,[4a] was between 398 nm in water and 414 nm in TBAQ24.

Ion-Exchange Equilibria. The fractions of IBA bound to latexes in 5.0 mM TAPS buffer solution at pH 9.10 were measured as follows. In a typical experiment, 5.0 mL of a solution of 5.0×10^{-4} M IBA in 5.0 mM pH 9.10 TAPS buffer was added to 5.0 mL of latex dispersion (0.200 mg mL^{-1}) in the same TAPS buffer. The dispersion was mixed by shaking for 5 s and after 15 min was ultrafiltered through a Millipore Millex-VV 0.1-μm membrane in a syringe. The first 2.5 mL of filtrate was collected in a 1-cm cuvette, and the amount of unbound IBA, $[IBA]_f$, was determined by UV spectrophotometry at 290 nm. The absorbance of IBA under these conditions depended linearly on concentration from 1.25×10^{-4} to 5.0×10^{-4} M. Each experiment was duplicated at least twice with less than 3% deviation in the value of $[IBA]_f$. Concentration of the particles in the dispersion by removal of 25% of the aqueous phase has little effect on the calculated selectivity coefficients. In blank experiments, UV spectra showed that the IBA concentration of the filtrate was identical with that of the original aqueous solution, indicating that there was no adsorption of IBA to the membrane filter. Also there was no detectable light scattering by the latex in the filtrates of dispersions, indicating that no latex particles passed through membrane.

The fractions of chloride ion in ultrafiltrates from latexes in 5 mM TAPS buffer at pH 9.1 were measured by the same general method using a chloride ion-selective electrode (Orion Model number 96-17B) as the detector.[4]

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(20) Starks, C. M.; Liotta, C. *Phase Transfer Catalysis*; Academic: New York, 1978; pp 60–64.