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Catalysis of Decarboxylation of 6-Nitrobenzisoxazole-3-carboxylate by Cationic Polymer Colloids

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Polystyrene latexes with quaternary ammonium ion-exchange sites catalyze the decarboxylation of 6-nitrobenzisoxazole-3-carboxylate in aqueous dispersions. A catalytic rate constant of 2.1×10^4 times the rate constant in water was achieved in particles containing 24 mol % of poly((styrylmethyl)-tri-*n*-butylammonium chloride) repeat units. This is the largest rate enhancement reported at 25 °C for decarboxylation of 6-nitrobenzisoxazole-3-carboxylate in any colloidal or polymeric medium. The decarboxylation kinetics fit both the enzyme model of micellar catalysis and an ion-exchange model. Added electrolyte decreases the rate of decarboxylation but increases the intrinsic catalytic rate constants in the more highly swollen latexes. The fraction of (styrylmethyl)trimethylammonium ion repeat units in the polymers has little effect on the rate of decarboxylation. The catalytic activity of the poly((styrylmethyl)trialkylammonium) ions in the latex increases in the order of increasing lipophilicity: Me < Et < Pr < Bu. The 200–350-nm diameter monodisperse colloidal particles with varied functional group content were prepared by emulsion copolymerization of styrene, (styrylmethyl)-trimethylammonium chloride, divinylbenzene, and (chloromethyl)styrene followed by reactions with trialkylamines to form the anion-exchange sites.

Introduction

Chemical reactions in aqueous colloidal dispersions are related to important reactions in living organisms, in chemical manufacturing, and in environmental waste treatment. Since reactions in living organisms take place in heterogeneous environments, association colloids such as micelles and bilayer vesicles have been considered as mimics for the natural environments of enzymes.[1] Hydrophobic and electrostatic interactions are major driving forces for the binding of substrates to enzymes and synthetic colloids and for catalysis by enzymes and synthetic colloids. In industry, too, chemical processes are carried out under heterogeneous conditions. Manufacturing processes using aqueous colloids rather than organic solvents would reduce the need for solvent recycling and disposal. Synthetic chemicals often find their way into environments on our planet where they threaten the lives of living organisms, including man. Understanding how chemical reactions are affected by colloidal media may aid understanding of the persistence or the degradation of pollutants in the heterogeneous environments of soils and natural waters. We are investigating catalyst supports composed of colloidal polymer particles of carefully controlled composition and size, with the aim of understanding how the hydrophobic and electrostatic interactions affect fundamental chemical reactions in heterogeneous aqueous environments.

One particularly useful reaction to probe catalytic effects of colloidal media is the unimolecular concerted decarboxylation of 6-nitrobenzisoxazole-3-carboxylate (1).[2] The reaction is not catalyzed by acids or bases, and its rate of decarboxylation is highly dependent on solvent: 10^8 times faster in hexamethylphosphoramide than in water. The concerted mechanism shown in Scheme I may apply also to many decarboxylation processes occurring in nature.[3] The decarboxylation of 1 is retarded by hydrogen bonding stabilization of the ground state and greatly accelerated by transition-state stabilization in nonpolar or polar aprotic solvents.[2c] It is accelerated markedly by enzyme mimics such as micelles,[4] bilayer vesicles,[4d,e] microemulsions,[5] polysoaps,[6] polymer and silica gels,[7] and poly(crown

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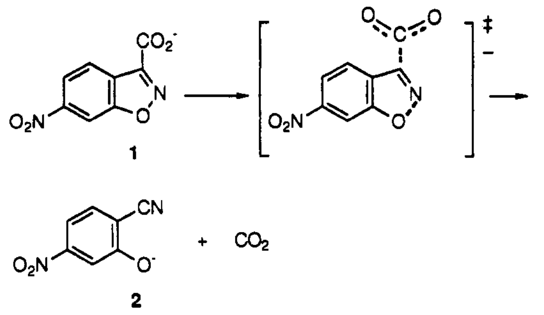
Scheme I



ethers)[8] and by catalytic antibodies.[9] The largest rate enhancements over the rate in water previously reported are 19 000 at 20 °C for catalytic antibodies, 14 000 at 25 °C for the CsCl complex of poly(vinylbenzo-18-crown-6) (P18C6), and 86 000 at 5 °C for CsCl·P18C6.

Colloidal polymer particles in water, also known as latexes, are produced by emulsion polymerization. Their typical diameters are 50–500 nm. They have great potential value for the study of fundamental heterogeneous reactions because of their high surface area, ease of synthesis, and ease of synthetic control of properties via hydrophile and lipophile content. Cross-linked polystyrene latexes have shown considerable promise as support materials for various catalysts,[10] but fundamental understanding of how latex structure affects the reactivity of bound molecules is still lacking. That understanding is needed for the rational design of new catalysts in aqueous media. In the present study, using the "shot–growth" emulsion copolymerization method,[11] we have prepared a series of uniform latex particles with systematic variation of hydrophile–lipophile balance by changing the anion-exchange capacity and the structure of the quaternary ammonium ion binding site, and we have examined the catalytic effects of the ion-exchange latexes in aqueous dispersions on the decarboxylation of 6-nitrobenzisoxazole-3-carboxylate.

Experimental Section

Materials. Styrene (Aldrich) and chloromethylstyrene (Dow Chemical Co. vinylbenzyl chloride {VBC}, 70/30 *m*/*p*) were distilled under reduced pressure and stored at −5 °C until use. Divinylbenzene (Polysciences Inc.) contained no methanol-insoluble component and was used as received. (Styrylmethyl)trimethylammonium chloride (STAC) was prepared from (chloromethyl)styrene and trimethylamine.[12] 2,2′-Azobis(*N*,*N*′-dimethyleneisobutyramidine) dihydrochloride (VA-044, Wako Chemicals) and trimethylamine (25 wt % in water), triethylamine, tripropylamine, tributylamine, and 5-(dimethylamino)naphthalene-1-sulfonic acid hydrate (Aldrich) were used as received. Methyl 6-nitrobenzisoxazole-3-carboxylate (Pfaltz & Bauer) was recrystallized from methanol to yield light yellow needles that were characterized by NMR and IR and had mp 130–131 °C (lit.[13] mp = 131–132 °C). 4-Nitroindole-2-carboxylic acid (mp 318–320 °C dec) was prepared by nitration[14] of ethyl indole-2-carboxylate (Aldrich) followed by hydrolysis,[15] and its structure was confirmed by IR and NMR spectra. Deionized distilled water was used throughout.

TMAQ14×1. In a 250-mL three-neck round-bottom flask, a solution of 108 mL of water and 0.072 g of STAC was stirred mechanically and flushed with argon for 15 min. A mixture of 11.0 g of styrene (ST), 0.15 g of divinylbenzene (DVB), and 1.0 g of chloromethylstyrene (CMS) was added, the stirred mixture was heated to 60 °C with an oil bath, and 0.12 g of VA-044 was added. A second flask was initially charged with 20 mL of water and 0.10 g of STAC and left for about 15 min with argon bubbling. Then, a mixture of 1.0 g of ST, 0.050 g of DVB, 3.0 g of CMS, and finally, 0.040 g of VA-044 was added and stirred at room temperature under argon for 5 min. The second monomer mixture was added to the first 1.5 h after initiation of the first mixture, and the combined mixture was stirred at 60 °C for 3 h. The latex was filtered through cotton to remove coarse particles. The chloromethyl groups of the latex were converted to quaternary ammonium ions by treatment with an excess of trimethylamine in a sealed 150-mL stainless steel vessel that was 3/4 immersed in a 62 °C oil bath for 100 h. The quaternized latex was ultrafiltered[10c] and washed with water until the filtrate reached a constant low conductivity (<10 μmho) to remove low molar mass solutes. A ^{13}C NMR spectrum of the swollen latex[16] showed no trace of CH_2OH groups that might arise from partial hydrolysis of chloromethyl groups during quaternization.

TMAQ39×1. The procedure for TMAQ14×1 was used except in the first stage 7.0 g of ST, 0.15 g of DVB, and 5.0 g of CMS were used and in the second stage 1.0 g of ST, 0.050 g of DVB, and 3.0 g of VBC were used.

TMAQ60×1. The procedure for TMAQ14×1 was used except in the first stage 3.0 g of ST, 0.15 g of DVB, and 9.0 g of CMS were used and in the second stage 1.0 g of ST, 0.050 g of DVB, and 3.0 g of CMS were used.

TBAQ24×1, TPAQ13×1, TEAQ32×1, and HEDMAQ25×1. The procedure and the same copolymer as for TMAQ39×1 were used except that in the quaternization step tri-*n*-butylamine, tri-*n*-propylamine, triethylamine, and *N*,*N*-dimethylethanolamine were used instead of trimethylamine.

6-Nitrobenzisoxazole-3-carboxylic acid was prepared by heating its methyl ester in 80% aqueous sulfuric acid on a steam bath for 20 min and then pouring the reaction mixture into ice–water.[4b,17] The white solid, after drying in vacuo, had mp 167–169 °C [lit.[17] mp 167–169 °C (monohydrate)]. A ^1H NMR spectrum showed 90 mol % carboxylic acid and 10% methyl ester. The crude product was recrystallized from a mixture of acetone and heptane to produce light yellow needles that were filtered and washed with chloroform. These crystals contained no methyl ester by ^1H NMR analysis and less than 5% of the decarboxylation product, 2-cyano-5-nitrophenoxide, by ^1H NMR analysis. They were used for kinetic studies without further purification.

Chloride Determination. A 1-mL sample of TMAQ14×1 (43.5 mg/mL) was diluted to 30 mL with deionized water, and 0.5 mL of 5 M $NaNO_3$ was added. The latex was titrated using an ORION chloride-selective electrode (Model 96-17B) with standard 0.025 N $AgNO_3$ solution, and the concentration of quaternary ammonium sites was calculated by the following equation: mmol of quaternary ammonium groups (N^+Cl^-) per g of dry latex = [0.025 mmol/mL][mL of consumed $AgNO_3$]/[g of latex].

Particle Sizes. The diameters of 50 nonaggregated particles were measured from TEM negatives using a microscope fitted

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Table I. Compositions and Sizes of Cationic Latexes

				diameter, nm					
				TEM[c]		DLS, d_h[d] in		swelling ratio $(d_h/d_w)^3$	
sample	N+ [a]/g	N+ [b]/mL	N+ (mol %)	d_w[e]	d_n[f]	2 mM NaOH	H_2O	2 mM NaOH	H_2O
TMAQ60×1[g]	3.41	0.894	60.8	215.8	214.3	348	423	4.2	7.5
TMAQ39×1	2.63	0.801	38.9	172.1	169.0	264	300	3.6	5.3
TMAQ14×1	1.15	0.752	14.3	185.0	183.9	220	225	1.7	1.8
TBAQ24×1[h]	1.60	0.879	23.7	187.1	184.2	236	258	2.0	2.6
TPAQ13×1[i]	0.92	0.552	13.4	162.8	161.7	198	208	1.8	2.1
TEAQ32×1[j]	2.13	0.578	31.6	165.5	164.2	264	314	4.1	6.8
HEDMAQ25×1[k]	1.66	0.582	24.6	165.3	164.6	242	275	3.1	4.6

[a] mequiv of N^+ per gram of dry latex. [b] mequiv N^+ per mL of swollen latex in 2 mM NaOH (calculated by using 1.10 g/cm^3 as the density of the dry latexes). [c] Fifty particles were measured on micrograph negatives. [d] Hydrodynamic equivalent diameter from dynamic light scattering. [e] Weight average diameter $d_w = [\sum N_i d_i^6/\sum N_i d_i^3]^{1/3}$. [f] Number average diameter $d_n = [\sum N_i d_i^3/\sum N_i]^{1/3}$. [g] TMA = trimethylammonium. [h] TBA = tri-*n*-butylammonium. [i] TPA = tri-*n*-propylammonium. [j] TEA = triethylammonium. [k] HEDMA = (2-hydroxyethyl)dimethylammonium.

with a micrometer scale.[18] Hydrodynamic equivalent diameters of latex particles in 2 mM NaOH solution and in pure water were obtained at 90° scattering angle in the single scattering limit with an ALV5000 photon correlator.

Kinetic Experiments and Calculations. A 0.0133 M stock solution of 6-nitrobenzisoxazole-3-carboxylic acid for kinetic measurements were prepared in ethanol containing 2 mM HCl on the day of use. A 2 mM NaOH solution (pH 11.3 ± 0.1) was prepared using nitrogen-purged water and was stored in an air-tight polyethylene container. The following kinetic run is typical. A 1-cm cuvette was filled with 3.0 mL of 2 mM NaOH solution, and 30 μL of 24.2 mg/mL TMAQ60×1 was added. The cuvette was stoppered and placed in the sample chamber of a Varian DMS-200 spectrophotometer thermostated at 25.0 ± 0.1 °C. After 15 min 30 μL of the substrate solution was added and mixed by rapidly shaking the cuvette for 2 s. The λ_{max} of the decarboxylation product, 2-cyano-5-nitrophenoxide, was 398 nm in water and 426 nm in latexes. Such a red shift in the absorption maximum of this compound was also reported by Klotz[6a] and by Smid.[8a] The first-order rate constants (k_{obsd}) for appearance of 2-cyano-5-nitrophenoxide were calculated by linear least-squares fitting of the integrated form of the first-order rate equation: $\ln(A_\infty - A_t) = \ln(A_\infty - A_0) - kt$, where A_t, A_0, and A_∞ refer to the absorbances at times t, 0, and ∞.[19] All correlation coefficient values were >0.999. The end point was usually determined after at least 8 half-lives, and the rate constant was usually calculated from data comprising the first 3 half-lives.

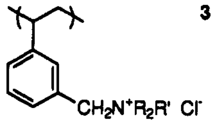
The slopes and intercepts of the double reciprocal plots used to determine k_c and K in the enzyme model and of the Arrhenius plots were determined by linear least-squares analysis assuming random errors only in the ordinates.

Measurements of 4-Nitroindole-2-carboxylate Binding. Mixtures of TBAQ24×1 ($N^+ = 1.41 \times 10^{-5}$ M) and varying amounts of 4-nitroindole-2-carboxylate were ultrafiltered through a Millipore Millex-VV 0.1-μm membrane in a syringe. All of the filtrate was collected, and the amount of carboxylate was determined by UV spectrophotometry.

Fluorescence spectra of 5-(dimethylamino)-1-naphthalenesulfonate[20] (5×10^{-6} M) in the presence of latexes were measured on a Spex model F112A spectrofluorometer at 23 °C in aqueous solutions adjusted to pH 8.50 with 0.02 M boric acid buffer.

Results

Particle Preparation. Using the shot–growth method,[11] a series of monodisperse latexes with systematic variation of hydrophile–lipophile balance was prepared by emulsion copolymerization of styrene, (styrylmethyl)trimethylammonium chloride, divinylbenzyne, and (chloromethyl)styrene. The copolymers were treated with trialkylamines to create large amounts of anion-exchange sites (structure 3).



3 : TMA, R = R' = CH_3
TEA, R = R' = CH_2CH_3
TPA, R = R' = $CH_2CH_2CH_3$
TBA, R = R' = $CH_2CH_2CH_2CH_3$
HEDMA, R = CH_3, R' = CH_2CH_2OH

The amount of the charged monomer used in the first stage of emulsion polymerization controls the number and size of particles, the divinylbenzene prevents high ion content polymers from dissolving as polyelectrolytes, and the amount of (chloromethyl)styrene controls the number of anion-exchange sites obtained after reaction with trialkylamines. The samples are described in Table I. In the notation TMAQ60×1, TMAQ means the copolymer was quaternized with trimethylamine, 60 refers to 60 mol percent of quaternary ammonium repeat units, and ×1 refers to 1 wt % divinylbenzene cross-linking at the copolymer stage. The number of ionic functional groups (N^+) was varied by the amounts of charged monomer and chloromethylstyrene used. The quaternized latexes were purified by ultrafiltration to remove possible low molar mass solutes until the filtrate reached a constant low conductivity. Measurements of the diameters of dry latex particles by transmission electron microscopy (TEM) and the hydrodynamic diameters by dynamic light scattering (DLS) are reported in Table I.[21] The polydipersity indexes d_w/d_n by TEM were less than 1.02.

Decarboxylation Kinetics. The decarboxylation of 1 in aqueous solution accelerated upon addition of cationic latexes as evidenced by rapid appearance of the yellow product, 5-nitro-2-cyanophenoxide (2). Typical plots of the first-order rate constants (k_{obsd}) for decarboxylation as a function of the concentration of latexes are shown in Figure 1a. The first-order rate constants (k_{obsd}) increase with the increase of latex concentration as substrate is incorporated into the latex and should become constant when the substrate is fully bound. We were unable to reach the fully bound limit because the turbidity in dispersions with larger amounts of particles prevented measurement of product absorbance.

The first-order rate constants determined at different latex concentrations were analyzed according to the Menger–Portnoy pseudophase model[22] as shown in Scheme II for latexes TMAQ60×1 and TMAQ39×1, where [latex],

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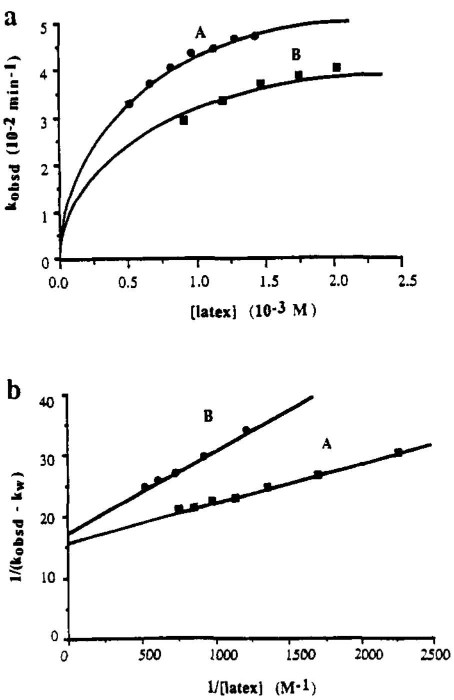
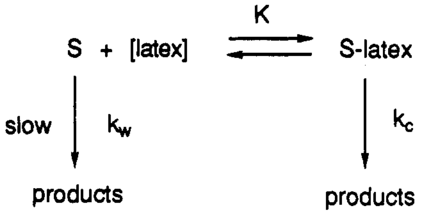


Figure 1. (a) Pseudo-first-order rate constants for decarboxylation of 1.3 × 10^{-4} M 6-nitrobenzisoxazole-3-carboxylate as a function of concentration of quaternary ammonium groups of TMAQ39×1 (A) and TMAQ60×1 latex (B) in 2 mM NaOH solution at 25.0 °C. (b) Plots used to determine k_c and K for decarboxylation by Scheme II.

Scheme II



$$1/(k_{obsd} - k_w) = 1/(k_c - k_w) K [\text{latex}] + 1/(k_c - k_w)$$

S and S–latex are the molar concentrations of quaternary ammonium groups of latexes, free substrate, and latex-bound substrate in the whole reaction mixture, K is the association constant of substrate to latex, k_w is the decarboxylation rate constant without latex, and k_c is the rate constant for the latex-bound species. Since k_w is obtained separately in the absence of the latex (1.84 × 10^{-4} min^{-1}), K and k_c of Scheme II can be determined by plotting $1/(k_{obs} - k_w)$ vs 1/[latex] (Figure 1b),[22] in which the decarboxylation rate constants, k_{obsd}, were measured at constant initial substrate concentration and varied excess of latex. Similar data using latex TBAQ24×1 are in Figure 2a. The rate constants do not appear to approach a maximum value, but a good linear double reciprocal plot was found as shown in Figure 2b. Table II reports the pseudo-first-order rate constants of decarboxylation in all of the latexes. Table III reports the binding constants and the intraparticle rate constants of decarboxylation by the latexes as well as other colloids and polymers. All of the latexes catalyze the decarboxylation in aqueous dispersions.

The temperature dependences of the rate constants in four different latexes are shown in the Arrhenius plots of Figure 3, and the activation parameters are reported in Table IV. The linearity of the plots indicates no major change in the fraction of 1 reacting in the particle phase over the range of temperature investigated.

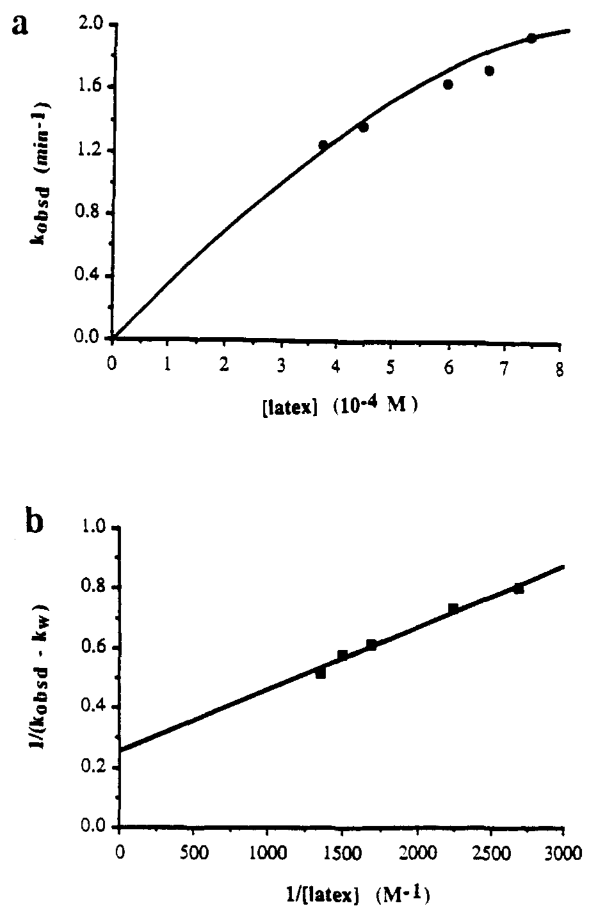


Figure 2. (a) Pseudo-first-order rate constants for decarboxylation of 6.58 × 10^{-5} M 6-nitrobenzisoxazole-3-carboxylate as a function of concentration of quaternary ammonium groups of TBAQ24×1 in 2 mM NaOH solution at 25.0 °C. (b) Plot used to determine k_c and K.

Table II. First-Order Rate Constants of Decarboxylation of 1 Catalyzed by Latexes at 25.0 °C

	1^a (10^{-5} M)	latex^b (mg/mL)	N$^{+\,c}$ (10^{-4} M)	$10^3 k_{obsd}{}^d$ (s^{-1})	$k_{obsd}/k_w{}^e$
TMAQ60×1	13.04	0.559	19.06	0.68	220
TMAQ39×1	13.04	0.500	13.16	0.79	250
TMAQ14×1	8.78	0.395	4.54	1.2	400
TEAQ32×1	6.58	0.619	13.20	2.5	800
TPAQ13×1	6.58	0.438	3.95	12.1	4000
TBAQ24×1	6.58	0.463	7.42	32.4	10500
HEDMAQ25×1	6.58	0.524	8.70	1.0	340

[a] Concentration of 6-nitrobenzisoxazole-3-carboxylate. [b] The maximum amount of latex used. [c] Concentration of quaternary ammonium unit. [d] Using 2mM NaOH. [e] The first-order rate constant in water was k_w = 3.1 × 10^{-6} s^{-1}.

The decarboxylation rate in the absence of latexes is insensitive to added electrolytes.[2b] However, the latex-catalyzed process is profoundly influenced by addition of electrolyte. The addition of low concentrations of NaCl to TMAQ60×1 and to TMAQ39×1 speeds up the reactions to a rate maximum when the concentrations of electrolyte and latex are approximately equal (Figure 4), and at higher NaCl concentrations the rate constants decrease to less than those in the presence of latex alone. The addition of NaCl to the TMAQ14×1 and to TBAQ24×1 inhibits catalysis even when its concentration is less than that of latexes (Figure 5). Figures 6a and 7a show plots of k_{obsd} in 20 mM NaCl solutions for decarboxylation as a function of the concentrations of TMAQ60×1, TMAQ39×1,

Table III. Binding Constants and Rate Constants of Decarboxylation of 1 at 25.0 °C

	$10^3 k_c$[a] (s^{-1})	k_c/k_w[b]	K (M^{-1})
TMAQ60×1	0.95[c]	310	1300
TMAQ39×1	1.0[c]	340	2600
TBAQ24×1	65[c]	21000	1200
cetyltrimethylammonium bromide[d]	0.387	130	
cetyltributylammonium bromide[e]	8.53	2800	2–5000
1-methyl-4-dodecylpyridinium iodide[f]	0.342	160	1160
tri-*n*-octylethylammonium methanesulfonate[g]	27	9000	5000
poly(4-vinylpyridine), 54% octyl subst[h]	1.1	157	4100
IER, 15% cross-linked, 54% N^+TEA[i]	8.4	1400	
IER, 2% cross-linked, 22% N^+TEA[i]	1.7	283	
IER, 2% cross-linked, 79% N^+TEA[i]	1.4	233	
poly(vinylbenzo-18-crown-6)[j]	42	14000	

[a] k_c = the intrinsic rate constant in the colloidal pseudophase. [b] In this study the first-order rate constant in water, $k_w = 3.1 \times 10^{-6}$ s^{-1}. [c] Correlation coefficients (r) in the Menger–Portnoy analysis of TMAQ60×1, TMAQ39×1, and TBAQ24×1 are 0.997, 0.998, and 0.988, respectively. [d] Reference 4b, $k_w = 3.0 \times 10^{-6}$ s^{-1}. [e] Reference 4i, $k_w = 3.0 \times 10^{-6}$ s^{-1}. [f] Reference 4f, $k_w = 2.1 \times 10^{-6}$ s^{-1}. [g] Reference 4g, $k_w = 3.0 \times 10^{-6}$ s^{-1}. [h] Reference 6d, $k_w = 7.0 \times 10^{-6}$ s^{-1}. [i] Reference 7d, IER = ion-exchange resin with poly((styrylmethyl)triethylammonium groups, $k_w = 6.0 \times 10^{-6}$ s^{-1}. [j] Reference 8a, $k_w = 3.0 \times 10^{-6}$ s^{-1}.

Table IV. Activation Parameters of Decarboxylation

	ΔH^* (kcal mol^{-1})	ΔS^*[a] (cal deg^{-1} mol^{-1})	γ[b]	ref
TMAQ60×1	18.8 ± 0.1	−10	1.000	*c*
TMAQ39×1	18.6 ± 0.3	−10	0.999	*c*
TMAQ14×1	17.5 ± 0.3	−13	0.999	*c*
TBAQ24×1	13.6 ± 1.0	−20	0.984	*c*
water	29.4	15		4b
cetyltrimethylammonium bromide	21.3	−3		4b
poly(vinylbenzo-18-crown-6)	16.1	−11		8a

[a] 25.0 °C. [b] Correlation coefficient of the Arrhenius plot. [c] This work.

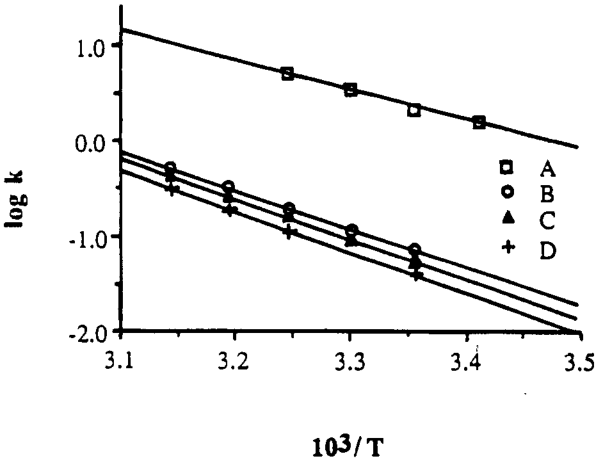


Figure 3. Plots of log k_{obsd} (in min^{-1}) vs $1/T$ in dispersions of TBAQ24×1 (A), TMAQ14×1 (B), TMAQ39×1 (C), and TMAQ60×1 (D) latexes.

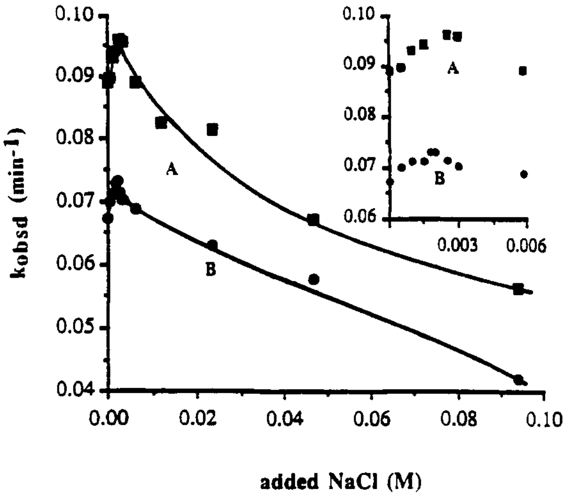


Figure 4. The effect of NaCl on k_{obsd} for decarboxylation of 1.31 × 10^{-4} M 6-nitrobenzisoxazole-3-carboxylate in 2 mM NaOH in the presence of latexes at 30.0 °C. A: TMAQ39×1 (0.50 mg/mL = 1.32 × 10^{-3} M N^+ groups). B: TMAQ60×1 (0.56 mg/mL = 1.91 × 10^{-3} M N^+ groups).

and TBAQ24×1, respectively. Figures 6b and 7b illustrate double reciprocal plots of ($k_{obsd} - k_w$) vs concentration of quaternary ammonium groups of TMAQ60×1, TMAQ39×1, and TBAQ2×1. The resulting rate constants and binding constants are in Table V.

Ion-Exchange Model. To gain further insight into the role of latex particles in the decarboxylation kinetics the data have been analyzed by an ion-exchange model. The model depends on some fundamental assumptions: (1) Ion exchange is much faster than chemical reaction. (2) The degree of dissociation of counter ions from the latex is negligible. (3) No excess substrate anions bind to the latex by nonspecific absorption. Assumptions 2 and 3 are equivalent to an assumption of stoichiometric binding: the charge of anions bound equals the charge of quaternary ammonium ions. The model is basically the same as the pseudophase ion-exchange model of micellar catalysis,[23] except that counterion dissociation from the latex is neglected and the latex is a true stable phase, not a pseudophase in which dissociation and association of surfactants is rapid compared with the rate of decarboxylation.

The fundamental equations of the model are a rate equation (1), ion-exchange selectivity coefficients $K_{S/Cl}$ (2) and $K_{OH/Cl}$ (3), and mass balance equations (4–7)

$$k_{obsd} = k_w S_f/S_t + k_c S_b/S_T \tag{1}$$

$$K_{S/Cl} = S_b Cl_f / S_f Cl_b \tag{2}$$

$$K_{OH/Cl} = OH_b Cl_f / OH_f Cl_b \tag{3}$$

$$S_T = S_b + S_f \tag{4}$$

$$L = Cl_b + S_b + OH_b \tag{5}$$

$$OH_T = OH_b + OH_f \tag{6}$$

$$Cl_T = L + [NaCl] = Cl_b + Cl_f \tag{7}$$

where k_{obsd} is the measured pseudo-first-order rate constant, k_w is the rate constant in the aqueous phase, k_c is the rate constant in the particle phase, all concentrations are based on total volume of dispersion, S_T is the analytical concentration of substrate in the dispersion, and S_f and S_b are the concentrations of substrate free in the aqueous phase and bound in the particles. This model does not

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[23] (a) Quina, F. H.; Chaimovich, H. J. *J. Phys. Chem.* **1979**, *83*, 1844. (b) Romsted, L. S. In *Surfactants in Solution*; Mittal, K. L., Lindman, B., Eds.; Plenum: New York, 1984; pp 1015–1068. (c) Quina, F. H.; Politi, M. J.; Cuccovia, I. M.; Baumgarten, E.; Martins-Franchetti, S. M.; Chaimovich, H. J. *J. Phys. Chem.* **1980**, *84*, 361.

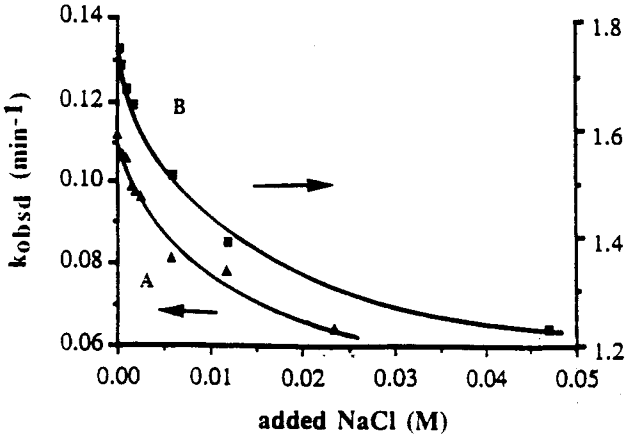

Figure 5. The effect of NaCl on k_{obsd} for decarboxylation of 8.78 × 10^{-5} M 6-nitrobenzisoxazole-3-carboxylate in the presence of TMAQ14×1 latex (A, 0.395 mg/mL = 4.54 × 10^{-4} M of N^+ groups, 30.0 °C) and of 6.58 × 10^{-5} M 6-nitrobenzisoxazole-3-carboxylate in 2 mM NaOH in the presence of TBAQ24×1 latex (B, 0.453 mg/mL = 7.26 × 10^{-4} of N^+ groups, 25.0 °C).

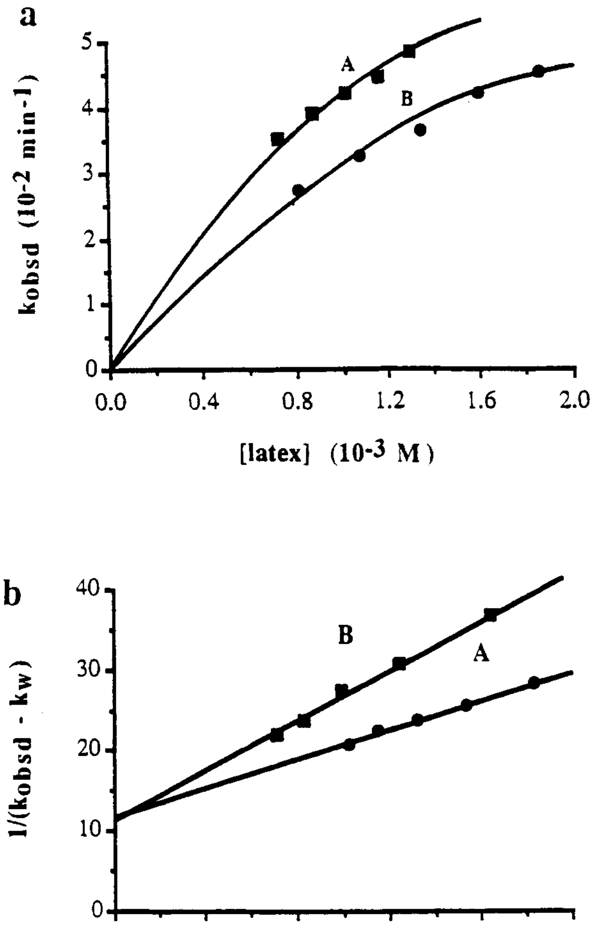

Figure 6. (a) Pseudo-first-order rate constants for decarboxylation of 1.3 × 10^{-4} M 6-nitrobenzisoxazole-3-carboxylate as a function of concentration of quaternary ammonium groups of TMAQ39×1 (A) and TMAQ60×1 latex (B) in 2 mM NaOH and 20 mM NaCl at 25.0 °C. (b) Plots used to determine k_c and K.

consider buffered solutions but could be extended to include them with appropriate equilibria and mass balances.[23]

Since k_w is determined independently, determination of the catalytic rate constant k_c and the two ion-exchange selectivity coefficients involves least-squares minimization of deviations from their calculated values. Since OH_T = 2 mM and Cl_T = 20 mM in data sets with excess added NaCl, and selectivity coefficients $K_{OH/Cl} \ll 1$ for cationic micelles[23] and for ion-exchange resins,[24,25] the binding of OH can be neglected and only k_c and $K_{S/Cl}$ must be evaluated. Results of those computer evaluations are in Table V. Despite high inverse correlation coefficients of

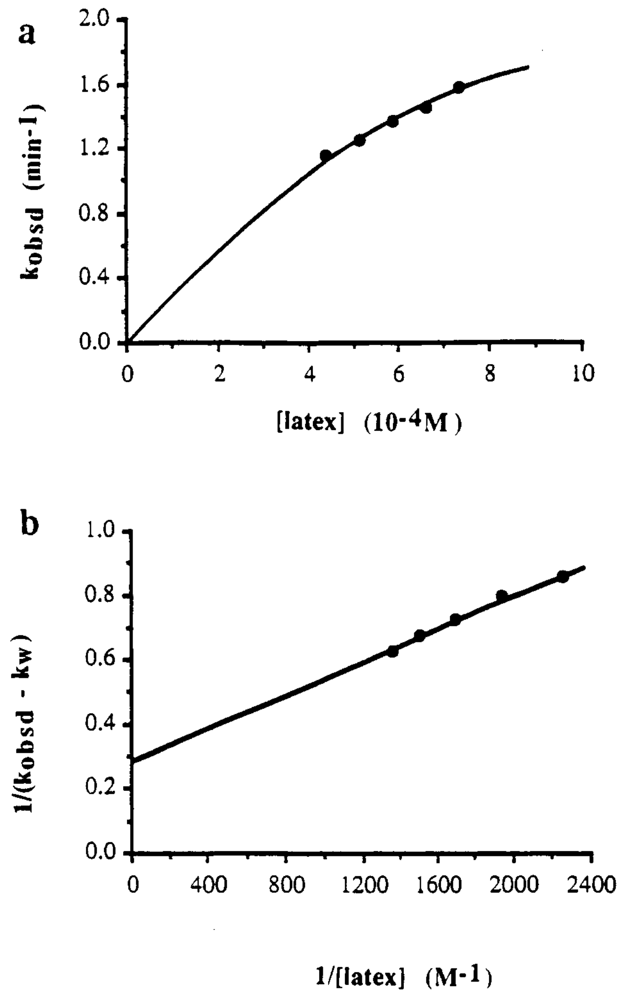

Figure 7. (a) Pseudo-first-order rate constant for decarboxylation of 6.58 × 10^{-5} M 6-nitrobenzisoxazole-3-carboxylate solution as a function of concentration of quaternary ammonium groups of TBAQ24×1 in 2 mM NaOH and 20 mM NaCl solution at 25.0 °C. (b) Plot used to determine k_c and K.

Table V. Binding Constants, Ion-Exchange Selectivity Coefficients, and Rate Constants of Decarboxylation of 1 by Latexes in NaCl Solutions[a]

	10^3k_c[b] (s^{-1})	K[c] (M^{-1})	r[d]	10^3k_c[e,g] (s^{-1})	$K_{S/Cl}$[f,g]
TMAQ60×1	1.50	530	0.994	1.5 ± 0.1	11 ± 2
TMAQ39×1	1.43	940	0.995	1.4 ± 0.1	21 ± 2
TBAQ24×1	58.2	1100	0.993	58 ± 5	24 ± 3

[a] In 2 mM NaOH and 20 mM NaCl solution. [b] Intrinsic rate constants calculated by the Menger–Portnoy pseudophase model. [c] Binding constants calculated by the pseudophase model. [d] Correlation coefficient of the linear least-squares fit in the pseudophase model analysis. [e] Intrinsic rate constants calculated by the ion-exchange model. [f] Ion-exchange selectivity coefficients for chloride ion and substrate anion calculated by the ion-exchange model. [g] Correlation coefficients of k_c and $K_{S/Cl}$ in the ion-exchange model were −0.994, −0.998, and −0.995 for the three data sets listed.

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(24) Helfferich, F. *Ion Exchange*; McGraw-Hill: New York, 1962; pp 100–125 and 250–319.

(25) The Dow Chemical Company, *Dowex: Ion Exchange*, 1964, p 75.

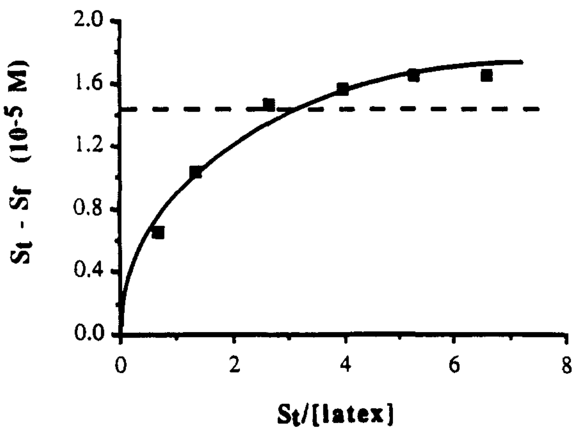

Figure 8. Binding of 4-nitroindole-2-carboxylate (4) to TBAQ24×1 latex. Plots of $S_t - S_f$ vs S_t/[latex]: S_t = initial concentration of 4 in 2 mM NaOH solution; S_f = concentration of 4 in filtrate; dashed line $S_t - S_f$ = [latex] = 1.41×10^{-5} M.

Table VI. Wavelengths of Fluorescence Maxima of DNS in the Latex Dispersions[a]

latexes	N^{+} [b] (10^{-4} M)	λ_{fmax} of DNS[c] (nm)
probe only		513
TMAQ60×1	18.6–5.89	472
TMAQ39×1	13.0–6.53	452
TMAQ14×1	4.50–2.26	449
TEAQ32×1	12.1–6.29	455
TPAQ13×1	3.90–1.95	441
TBAQ24×1	7.33–3.69	443
HEDMAQ25×1	8.44–4.28	454
CTABr		480[d]
TEAQ79		482[d]

[a] The solutions were adjusted to pH 8.50 with 0.02 M borate buffer. [b] Concentration of quaternary ammonium unit. [c] Concentration of DNS = 5×10^{-6} M; excitation wavelength = 320 nm, error limits ±1 nm. [d] Reference 20a. CTABr = cetyltrimethylammonium bromide; TEAQ79 = polyelectrolyte with 79 mol % (styrylmethyl)triethylammonium chloride and 21% styrene repeat units.

k_c with $K_{S/Cl}$, the Marquardt method found reasonable least-squares minima. When there is no excess added NaCl, the binding of OH cannot be neglected.

We tested the assumption of stoichiometric binding of substrate experimentally by measuring spectrophotometrically the binding of 4-nitroindole-2-carboxylate (4) as a model heteroaromatic carboxylate of about the same size and polarity as the reactive anion 1, to the most lipophilic of the latexes, TBAQ24×1. The binding curve in Figure 8 shows organic anion binding in excess of the stoichiometric amount only when the molar concentration of organic anion substantially exceeds the molar concentration of quaternary ammonium ions in the latex.

Fluorescent Probe. As an independent probe of the polarity at the binding sites in the latexes the fluorescence spectrum of 5-(dimethylamino)naphthalene-1-sulfonate[20] (DNS) was measured in each latex. A ratio of quaternary ammonium groups to DNS of at least 25 was used to ensure complete binding of DNS, and the emission maxima were independent of concentration of particles over a 2-fold range as shown in Table VI.

Discussion

The latex particles used for kinetic studies in 2 mM NaOH solution are 200–350 nm in diameter, 50 times larger than typical micelles, reverse micelles in a microemulsion, or synthetic polyelectrolytes in solution, and 2000 times smaller than typical ion-exchange resin beads. Unlike micelles, all of the ionic functional groups of a latex are covalently bound. The larger sizes found by DLS than by TEM show that the particles are swollen in aqueous dispersions. In water our 1% cross-linked latex with the highest ion-exchange capacity, TMAQ60×1, swells to about seven times its dry volume, while ones with the fewest ionic groups swell to about two times their dry volumes (Table I). The particles with higher ion-exchange capacities were more swollen in pure water than in 2 mM NaOH solution, as expected for slightly cross-linked ion-exchange resins.[24]

Saturation kinetic curves, as shown in Figures 1a and 2a, have been observed in micellar,[4b] bilayer membrane,[4d] polysoap,[6d] polyethylenimine,[6a] and poly(crown ether)[8a] catalysis of decarboxylation of 1. The intrinsic rate constants even in the most hydrophilic latexes TMAQ60×1 and TMAQ39×1 (Table III) are 300 times greater than in water, about the same as in ethanol ($k_{EtOH} = 1.0 \times 10^{-3}$ s^{-1}, at 30 °C),[2b] and more than twice as large as in the typical cationic amphiphile, hexadecyltrimethylammonium bromide (CTABr).[4b] The ion-exchange capacity of the trimethylammonium ion (type-I anion-exchange resin) and the hydroxyethyldimethylammonium ion (type-II anion-exchange resin)[24,25] structure of the active site have only slight effects on the rate of decarboxylation (Table II). On the other hand, more lipophilic poly((styrylmethyl)trialkylammonium) ions greatly increase the catalytic activity of the latex in the order Me < Et < Pr < Bu. The catalytic rate constant in the more lipophilic poly((styrylmethyl)tributylammonium) ion latex TBAQ24×1 is greater than that in benzene, dioxane, and dichloromethane and is almost the same as in diethyl ether (9.0×10^{-2} s^{-1}, at 30 °C).[2b] The high activity of the lipophilic TBAQ24×1 is due entirely to the intrinsic rate constant k_c, not to the binding constant in the enzyme kinetic model (Table III) or to the selectivity coefficient in the ion-exchange model (Table V). The huge solvent effects on the rate of decarboxylation of 1 are due partly to destabilization of the ground state of anion 1 in non-hydrogen-bonding solvents and partly to stabilization of the transition state of the reaction by polar aprotic solvents, such as HMPA in which decarboxylation of 1 is 10^8 times faster than in water.[2] It is well-known from phase-transfer catalysis that tetralkylammonium counterions in aprotic media greatly increase the nucleophilicity of carboxylate anions relative to their reactivity in hydrogen-bonding solvents, mainly by raising the energy of the ground state.[26] We suggest that less hydration of the ground state is also the major cause of higher reactivity of 1 in TBAQ24×1. The large ionic radius of the poly((styrylmethyl)tributylammonium) compared with the smaller poly((styrylmethyl)trimethylammonium) ion reduces its ion–dipolar attraction for water so that the anion 1 binds in a much less aqueous environment. The activity of 1 is like that of a tetra-*n*-butylammonium or tri-*n*-octylmethylammonium carboxylate in benzene during phase-transfer catalysis. The dielectric constant and solubility parameter of polystyrene are similar to those of benzene.[27] The same effect is known for trimethylammonium and tributylammonium surfactant head groups in micellar catalysis (Table III).

The rate constants of decarboxylation of 1 and the wavelengths of maximum emission of DNS provide independent measures of the polarity of the binding sites

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(26) Starks, C.; Liotta, C. *Phase Transfer Catalysis*; Academic: New York, 1978.

(27) Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd ed.; John Wiley & Sons: New York, 1989. The dielectric constant (ϵ) and solubility parameter (δ (cal/mL)$^{1/2}$) of polystyrene are 2.49–2.55 and 9.1, respectively.

in the latexes.[20] The data in Table VI show that the particles with highest ion content, TMAQ60×1, have the most hydrated binding sites, and the particles with the most lipophilic quaternary ammonium ions, TPAQ13×1 and TBAQ24×1, have the least hydrated binding sites, but there is surprisingly little difference of fluorescence maxima among the rest of the latexes having 14–39% of ionic functional groups. The data in Table VI do indicate that all of the latexes have less aqueous binding sites than CTABr micelles and a poly((styrylmethyl)triethylammonium chloride) polyelectrolyte.

Results in Table IV show that the rate increase in the presence of latexes is due to a decrease of $\Delta H^{\ddagger}$ partly counteracted by a decrease of $\Delta S^{\ddagger}$, similar to the effect of poly(vinylbenzo-18-crown-6).[8a] Although our latex TBAQ24×1 gives the greatest rate enhancement at 25 °C, the CsCl complex of poly(vinylbenzo-18-crown-6) would have a higher rate constant at higher temperatures due to its higher $\Delta H^{\ddagger}$ and less negative $\Delta S^{\ddagger}$.

The ion-exchange model is needed for understanding of the effects of salts on the decarboxylation reactivity. First, let us analyze the basic assumptions of the model: (1) Ion exchange is much faster than chemical reaction, so that the latex always contains equilibrium amounts of anions. In ordinary ion-exchange with resins >100 μm in diameter, equilibrium of small ions between aqueous and resin phases is reached on a time scale of seconds.[24] Since our particles are 200–350 nm in diameter, slow ion exchange cannot limit rates of reaction. This assumption applies also to the enzyme-like model.

(2) The fraction of anions dissociated from the latex is negligible. Hexadecyltrimethylammonium chloride micelles typically have a degree of dissociation of about 0.3. More hydrophilic anions, such as hydroxide, have higher degrees of dissociation, and more lipophilic organic anions have lower degrees of dissociation from micelles. There must also be partial dissociation of counterions from the surface of latex particles to account for charge stabilization of the colloid. However, most of the ionic groups of the latexes in this investigation are located inside the particles. If a 300-nm diameter particle is treated as a hard sphere with each polymer repeat unit occupying a cube 0.55 nm on a side, only 1% of the repeat units lie on the surface[28] and only a fraction of the surface will be dissociated. There is no significant degree of dissociation of counterions from the interior of an ion-exchange resin.[24] Electrophoretic light scattering measurements of similar latex samples lead to calculation of ζ potentials of only 20–50 mV, indicative of low net charge of the particles, over the entire range of samples studied here.[29] Thus, the assumption of stoichiometric binding of counterions is approximately correct.

(3) No excess substrate anions bind to the latex by nonspecific sorption. Although the data in Figure 8 indicate that this assumption is not strictly true, binding of 4-nitroindole-2-carboxylate (a good model for 1) in excess of the stoichiometric amount occurs only when the concentration of organic anion (S_T) substantially exceeds the concentration of quaternary ammonium ions (L) in the latex. Since all kinetic experiments analyzed by the ion exchange model were performed with $S_T \ll L$, and the ion-exchange model gives excellent agreement of catalytic rate constants with the non-specific enzyme-like model, this assumption appears reasonable.

Now let us compare the results of the ion-exchange model with the results of the enzyme model. The data in Table V lead to the following conclusions. (1) The ion-exchange model and the nonspecific binding model of Scheme II give the same catalytic rate constant k_c. (2) The ion-exchange selectivity coefficient for the substrate relative to chloride ion does not depend greatly on the ion-exchange capacity of the TMA latexes. There was a high inverse correlation of k_c with $K_{S/Cl}$, but it did not prevent determination of k_c with reasonable confidence.

Figure 4 shows a limitation of the ion-exchange model. Increase of the concentration of chloride ion should lead to systematic decrease of k_{obsd}, as is the case at [NaCl] > 3 mM, if the k_c and/or $K_{S/Cl}$ does not vary with NaCl concentration. However, at low concentrations of added NaCl the k_{obsd} actually increases. We attribute that increase to deswelling of the latexes by added electrolyte, which reduces the water content of the latex interior and consequently increases k_c. Deswelling is due to osmotic forces and to replacement of the more hydrated hydroxide ion by the less hydrated chloride ion in the polymer upon addition of NaCl to the dispersion.[24] The effects of added electrolyte on swollen particle size are shown by the comparative hydrodynamic diameters in water and in 2 mM NaOH in Table I. The TMAQ14×1 and TBAQ24×1 latexes, which swell much less in the first place, do not show the increase in rate constant with low added amounts of NaCl (Figure 5) because the electrolyte has much less effect on their swollen sizes. Rate maxima with added salts in cationic micelles have also been reported.[4j]

Conclusions

Ion-exchange latexes having poly((styrylmethyl)trialkylammonium) ion binding sites greatly accelerate the rate of decarboxylation of 6-nitrobenzisoxazole-3-carboxylate (1). The rate enhancement of $k_c/k_w = 21\,000$ at 25 °C by the poly((styrylmethyl)tri-n-butylammonium) ion latex is greater than that of any colloidal or polymeric medium previously investigated. The catalytic activities of the latexes are due primarily to lesser hydration of the ground state of the reactant than in water. Alternative nonspecific binding and ion-exchange models of the kinetics lead to the same catalytic rate constants, and the ion-exchange model explains well the depression of rates by added electrolyte that competes with substrate for latex binding sites.

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(28) Ford, W. T. In *Chemically Modified Surfaces*; Mottola, H. A., Steinmetz, J., Eds.; Elsevier: Amsterdam, 1992; pp 155–172.

(29) Ackerson, B. J.; Davis, K.; Dubin, P.; Ford, W. T.; Yu, H., manuscript in preparation.