Polymerized Surfactant Vesicles: Effects of Polymerization on Intravesicular Ester Hydrolysis

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Abstract: Rate enhancements of the base hydrolysis of *p*-nitrophenyl laurate, PNPL, in the presence of surfactant and polymerized surfactant vesicles have been described in terms of the distribution of the reactants between water and vesicles. Binding constants for the association of PNPL and OH^- with nonpolymerized ($K_{PNPL} = 1.3 \times 10^4\ M^{-1}$, $K_{OH^-} = 1.8 \times 10^3\ M^{-1}$) and polymerized ($K_{PNPL} = 5.4 \times 10^3\ M^{-1}$, $K_{OH^-} = 3.6 \times 10^3\ M^{-1}$) vesicles calculated from kinetic treatments of the obtained rate constants agreed well with those determined independently from solubility ($K_{PNPL} = 1.8 \times 10^4$ and $4.8 \times 10^3\ M^{-1}$ for nonpolymerized and polymerized vesicles) and pH measurements ($K_{OH^-} = 2.7 \times 10^3$ and $2.4 \times 10^3\ M^{-1}$ for nonpolymerized and polymerized vesicles). These results were rationalized in terms of complete distribution of both PNPL and OH^- in both sides of nonpolymerized and polymerized vesicles at time scales faster than the hydrolysis. Aminolysis of PNPL by ethylenediamine, EDA, in the presence of surfactant and polymerized vesicles resulted in biphasic kinetics which were resolved into fast, k_{fast}, and slow, k_{slow}, components. Increasing EDA concentrations increased both k_{fast} and k_{slow}. This rate enhancement was two orders of magnitude more effective for nonpolymerized than polymerized vesicles. In nonpolymerized vesicles 90% of PNPL reacted with EDA. Conversely only 50% of PNPL could react with EDA in polymerized vesicles. These results were discussed in terms of different reaction sites in nonpolymerized and polymerized vesicles.

Surfactant vesicles[1,2] and their polymerized counterparts[3-5] represent the most sophisticated membrane mimetic agents.[6] They are increasingly utilized in reactivity control,[1,4,6,7] recognition,[3] solar energy conversion,[1,4,8-12] and drug delivery[13-15] and as models for biomembranes[16] and polymerization kinetics.[17] These utilizations are based on the abilities of vesicles to organize molecules within their environments. Reactants can be entrapped in the aqueous inner compartments, attached to the inner or outer surfaces, or intercalated in the vesicle bilayers. At the extreme, sites of chemical reactions can be restricted to the inner or outer surfaces of vesicles or to any space between them. Site control has been achieved by using chemically dissymmetrical surfactant vesicles[18-20] or by taking advantage of different binding sites[21,22] in, and different reagent permeabilities across, symmetrical vesicles.[23-26]

Much of our understanding of site-selective reactivities in vesicles is due to the pioneering work of Moss and his co-workers.[23-26] They have delineated endovesicular[23,24] (reactions occurring at the interior of vesicles), exovesicular[23,24] (reactions occurring at the exterior surface of vesicles), and transvesicular[25] (reactions whose rate is limited by the diffusion of the reagent across the bilayer of the vesicles) reactivities both in nonfunctional and functional surfactant vesicles. Cleavage of *p*-nitrophenyl acetate by thiol-functionalized vesicles, resolved into a fast and a slow process, was attributed to exovesicular and endovesicular reactions, respectively.[23] Similarly, the biphasic kinetics obtained in the hydrolysis of diphenyl *p*-nitrophenylphosphate in nonfunctional vesicles were rationalized in terms of exo- and endovesicular reactions.[24] Conversely, oxidation of vesicle entrapped 2-nitro-5-thiolatobenzoate (Ellman's anion) by the exovesicular *o*-iodosobenzoate ion was limited by the permeation of the reagent across the vesicles.[25] Careful manipulation of reagents and vesicles provides, therefore, a fine tuning of reactivities.

Polymerization stabilizes surfactant vesicles and allows a degree of permeability control.[4,5] Effects of polymerization on intravesicular reactivities are reported in the present work.

Experimental Section

p-Nitrophenyl acetate (PNPA, Aldrich) was recrystalized twice from chloroform. *p*-Nitrophenyl laurate (PNPL, Sigma) was used as received. Ethylenediamine (EDA, Fisher) was vacuum distilled just prior to use. All contact with air was carefully avoided. Fluorescamine (Addrich) was used as received. Preparation, purification, and characterization of $[n\text{-}C_{15}H_{31}CO_2(CH_2)_2]_2N^+(CH_3)(CH_2C_6H_4CH{=}CH_2)$, Cl^- (**1**) have been described.[17] All other chemicals (the best available reagent grade) were used as received. Water was purified by deionization and subsequent distillation in an all-glass apparatus.

Vesicles were prepared by ultrasonic dispersal of aqueous **1**. Typically, 10 mg of **1** was dispersed in 10 mL of H_2O (or aqueous NaOH) at 76 °C and at 150 W for 25 min by a Bransonic sonicator. Sonicated vesicles were passed through a Sephadex G-50 column prior to use. Concentrations of **1** were determined spectroscopically taking $\epsilon_{265nm} = 6 \times 10^3\ M^{-1}\ cm^{-1}$.[17] Vesicles were polymerized by irradiation by an Oriel 450

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Table I. Rate Constants for the Hydrolysis of *p*-Nitrophenyl Acetate in Vesicles and in Polymerized Vesicles Prepared from **1** at 25.0 °C[a]

$10^5[\mathbf{1}]$, M	k_2, M^{-1} s^{-1} in nonpolymerized vesicles	k_2, M^{-1} s^{-1} in polymerized vesicles
0	14.8	14.8
2.35		14.2
4.19	11.5	14.2
8.38	9.6	12.2
16.8	8.2	9.9
33.5	5.2	4.05

[a] At stoichiometric concentrations [PNPA] = 5.0×10^{-5} M and [NaOH] = 1.3×10^{-3} M.

W Xenon lamp under N_2 bubbling. The extent of polymerization was monitored spectrophotometrically by following the disappearance of styrene absorbances.[17]

Solubilities of PNPA and PNPL in water and in vesicles prepared from **1** prior and subsequent to polymerization were determined in equilibrated saturated solutions of the esters at 25.0 °C. The equilibrated solutions (typically after 5 days) were filtered and diluted by acetone and NaOH (0.1 mL of vesicles + 5.0 mL of acetone + 4.9 mL of 0.5 N NaOH), and the concentrations of phenolate ions were determined absorption spectrophotometrically. Known concentrations of the phenolate ions in appropriate vesicle solutions were utilized for calibrations.

Partitioning of EDA between water and **1** vesicles was determined by quantitative ultrafiltration with use of the Amicon MMC ultrafiltration system, at 20 lb/m^2 of pressure, and an Amicon Diaflow YM10 25-mm membrane. Concentrations of EDA in the filtrate were determined fluorometrically by using fluorescamine. Two milliliters of 0.01 M borate filter, pH 10, was mixed with 1.0 mL of the filtrate and then a 1.0 mL of 2.0×10^{-3} M acetone solution of fluorescamine was added with rapid stirring. Fluorescence intensities were determined on a SPEX Fluorolog. Fluorescence intensities increased with the filtrate volume. Ratios of vesicle bound to free EDA were calculated from the differences of initial fluorescence intensity vs. filtrate volume plots in the presence and in the absence of vesicles.

Reaction rates were monitored by following the time dependence of phenolate ion appearance spectrophotometrically at 400 nm in the thermostated compartment of a Cary 118C spectrophotometer. Good first-order plots were obtained for the hydrolyses. Aminolyses were resolved into two consecutive first-order plots (see Results).

Hydrodynamic radii of vesicles were determined by dynamic laser light scattering. A Malvern 2000 light-scattering system and a Spectra Physics 171 Ar^+ laser were used.[17] Typical sampling times were 0.5–3 μs. *Q* values (polydispersities) were in the range of 0.2–0.5.

A Radiometes pHM pH meter was used for adjusting and determining hydrogen ion concentrations.

Results

The rate constant, k_2, for the hydrolysis of *p*-nitrophenyl acetate, PNPA, showed only a modest decrease in the presence of surfactant vesicles prepared from **1**. Addition of increasing amounts of nonpolymerized **1** and polymerized **1** vesicles decreased k_2 values exponentially (Table I). This rate decrease is a consequence of partitioning of the reagents between the vesicles and water. Solubility determinations led to binding constants of 375 and 220 M^{-1} for the interaction of PNPA with nonpolymerized **1** and polymerized **1** vesicles (Figure 1). Under the conditions of the kinetic experiments less than 10% of PNPA associates with the vesicles. Conversely, hydroxide ion substantially binds to both nonpolymerized **1** (K = 2700 M^{-1}) and polymerized **1** (K = 2400 M^{-1}) vesicles (Table II). PNPA hydrolysis occurs, therefore, predominantly in bulk water. The apparent rate decrease is the consequence of the removal of some of the hydroxide ions from bulk water by the positively charged **1** vesicles.

Increased binding of *p*-nitrophenyl laurate, PNPL (Figure 1), manifested in enhanced rate constants for its hydrolysis in the presence of vesicles and polymerized vesicles prepared from **1** (Table III). Binding constants of 1.1×10^4 and 4.8×10^3 M^{-1} have been obtained from Figure 1 for the interaction of PNPL with nonpolymerized **1** and polymerized **1** vesicles, respectively. Rates of *p*-nitrophenolate ion appearance, both in nonpolymerized and polymerized vesicles, followed first-order kinetics over 3 half-lives. In all cases, greater than 90% substrate conversion could be ascertained. Co-sonication of PNPL with **1**, or injection of PNPL stock solutions to already formed vesicles, led, at same concentrations of **1**, to identical rate constants.

Addition of PNPL did not alter **1** vesicles. Dynamic light scattering (mean of four independent determinations, each within

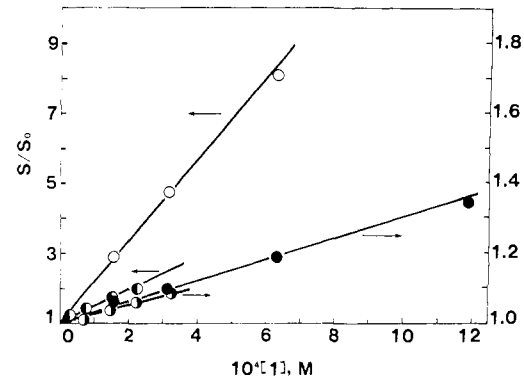

Figure 1. Solubility ratios of PNPL in nonpolymerized (○) and polymerized (◐) vesicles and solubility ratios of PNPA in nonpolymerized (●) and polymerized (◑) vesicles as functions of the surfactant concentration.

Table II. Hydroxide Ion Binding to Vesicles Prepared from **1**

$10^5[1]$, M	$10^4[OH^-]_{free}$,[a] M	$10^4[OH^-]_{bound}$,[b] M	$10^{-3}K$,[c] M^{-1}
	Nonpolymerized Vesicles		
0	12.9 12.9		
2.51	11.5	1.4	4.7
4.19	11.4	1.5	3.1
8.38	10.7	2.2	2.5
16.8	9.1	3.8	2.5
33.5	6.0	6.9	3.4
		K_{mean}	2700 M^{-1}
	Polymerized Vesicles		
0	13.2		
2.51	12.3	0.9	2.9
4.19	12.5	0.7	1.3
8.38	11.2	2.0	2.1
16.8	8.7	4.5	3.1
33.5	3.6	9.6	7.9
		K_{mean}	2400 M^{-1}

[a] Determined by a meter equipped with high alkaline sensitive electrodes. [b] Difference between total base − free base = vesicle bound base. [c] Vesicle–OH binding constant.

Table III. Rate Constants for the Hydrolysis of *p*-Nitrophenyl Laurate in Vesicles and Polymerized Vesicles Prepared from **1** at 25.0 °C[a]

$10^5[\mathbf{I}]$, M	10^3k_2, M^{-1} s^{-1} in nonpolymerized vesicles	10^3k_2, M^{-1} s^{-1} in polymerized vesicles
0	4.0	4.0
7.3		17.8
8.4	47.8	
9.1		18.5
12.5	68.3	
14.6		19.2
16.7	71.6	
18.3		21.7
25.1	90.6	
27.4		18.3
32.5		30
33.4	76.7	18.3
36.5		
66.8	54.2	

[a] At stoichiometric concentrations [PNPL] = 5.0×10^{-5} and [NaOH] = 1.3×10^{-3} M.

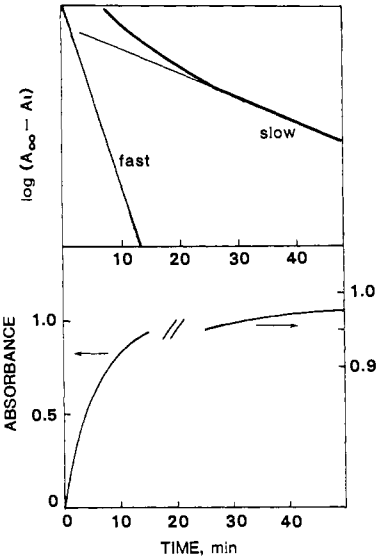

Figure 2. Typical plot of absorbances at 450 nn against time for the aminolysis of PNPL by EDA in nonpolarized **1** vesicles (lower half) and the resolution of the kinetic data into a fast and a slow component (top half).

Table IV. Aminolysis of *p*-Nitrophenyl Laurate in the Presence of Nonpolymerized Surfactant Vesicles Prepared from **1** at 25.0 °C[a]

10^4[EDA], M	10^4k, s^{-1}		pH[b]
	k_{fast}	k_{slow}	
0.47	17.1	2.25	4.89
0.83	69.3	11.3	6.07
1.25	134	34.8	6.74
1.67	33.6	70.7	7.13
2.67		254	
2.83	845	200	7.48
3.00		304	7.64

[a] At stoichiometric concentrations [PNPL] = 2.5×10^{-5} M and [1] = 6.7×10^{-4} M. [b] Bulk pH measured after the addition of EDA.

8% of the mean) yields 1103 Å for the hydrodynamic diameters of **1** vesicles prior and subsequent to the addition of PNPL.

Aminolysis of PNPL by ethylenediamine, EDA, in **1** vesicles is quite different. Appearances of *p*-nitrophenolate ion, unlike those in the hydrolysis, were found to be biexponential (Figure 2). Rate constants for the aminolysis could be resolved into a fast, k_{fast}, and a slow, k_{slow}, component for both nonpolymerized and polymerized vesicles. Data for nonpolymerized vesicles are given in Table IV. Increasing EDA concentrations increased, as expected, the rate constants of both the fast and slow processes. Increasing concentrations of [**1**], at given EDA concentrations, increased the aminolysis rates up to three orders of magnitude (Figure 3). Importantly, nonpolymerized **1** vesicles enhanced the rates of aminolysis at least two orders of magnitude more than polymerized ones (Figure 3).

Aminolysis of PNPL was also investigted as a function of increasing amounts of polymerizations of **1** vesicles (Table V). Increasing the extent of vesicle polymerization is seen to decrease the aminolysis rates down to 50% cross-linking to the styrene in the vesicles. Further polymerization had no effect on the aminolysis rate. Significantly, increasing the extent of vesicle polymerization led to a decrease of the percentage of PNPL conversion. In polymerized **1** vesicles only 50% of PNPL could react. Addition of NaOH, however, liberated all *p*-nitrophenyl laurate (Table V).

Binding constants for the interaction of EDA with nonpolymerized **1** and polymerized **1** vesicles were determined to be 1.1×10^3 and 1.0×10^3 M^{-1}, respectively, from ultrafiltrations. Under our experimental conditions EDA reacts as the monocation, $NH_2(CH_2)_2N^+H_3$.

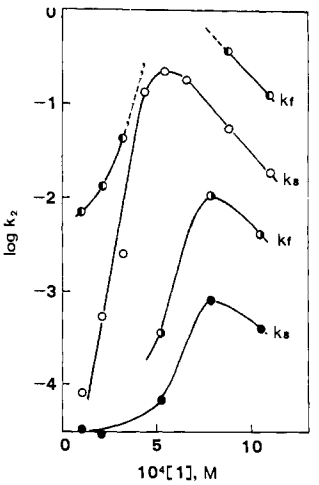

Figure 3. Plots of the fast, k_f, and slow, k_s, components of the rate constants for PNPL aminolysis as a function of EDA concentrations in nonpolymerized (◐, ○) and polymerized (◑, ●) **1** vesicles.

Table V. Effects of Vesicle Polymerization on the Aminolysis of *p*-Nitrophenyl Laurate at 25.0 °C[a]

vesicle polym,[b] %	10^3k, s^{-1}		pH[c]	PNPL conversion, %	
	fast	slow		end of reaction	after addition of NaOH[d]
0	84	20	7.48	87	87
5.2	82	19	7.75	92	97
17.2	19.3	3.7	7.40	91	93
22	6.2	1.2	5.8		
29	9.6	1.9		82	90
45	1.9	0.48	6.8	58	90
59	2.4	0.50	6.65	51	95
100	2.5	0.47	7.01	49	95

[a] Stoichiometric concentrations [PNPL] = 2.5×10^{-5} M, [EDA] = 2.83×10^{-3} M, and [1] = 6.7×10^{-4} M. [b] Percent of styrene conversion to polymer by photolysis, determined absorption spectrophotometrically. [c] Bulk pH after addition of EDA. [d] To pH 12.

Discussion

Hydrolysis of PNPL. Rate constants for the hydrolysis of PNPL in the presence of nonpolymerized **1** and polymerized **1** vesicles, k_M, can be treated by considering the reactions occurring in bulk water and in the environments of vesicles:

$$(\text{PNPL} + \text{OH}^-)_w \xrightarrow{k_w} \text{products} \quad (1)$$

$$(\text{PNPL} + \text{OH}^-)_M \xrightarrow{k_M} \text{products} \quad (2)$$

where the subscripts w and M refer to bulk water and to the pseudophase associated with the membrane mimetic agents (vesicles). The overall hydrolysis rate is described by

$$R_{total} = k_M[\text{PNPL}]_M[\text{OH}^-]_M[\mathbf{1}]\bar{V} + k_w[\text{PNPL}]_w[\text{OH}^-]_w(1 - [\mathbf{1}]\bar{V}) \quad (3)$$

where $\bar{V}$ is the molar volume of the surfactant in the vesicles and the concentrations of the reagents are given by

$$[\text{PNPL}]_{total} = [\text{PNPL}]_M[\mathbf{1}]\bar{V} + [\text{PNPL}]_w(1 - [\mathbf{1}]\bar{V}) \quad (4)$$

$$[\text{OH}^-]_{total} = [\text{OH}^-]_M[\mathbf{1}]\bar{V} + [\text{OH}^-]_w(1 - [\mathbf{1}]\bar{V}) \quad (5)$$

if reactions 1 and 2 do not affect the parttion equilibria:

$$[\text{PNPL}]_w \rightleftharpoons [\text{PNPL}]_M \quad (6)$$

$$[\text{OH}^-]_w \rightleftharpoons [\text{OH}^-]_M \quad (7)$$

and if both PNPL and OH^- appreciably bind to the vesicles, then

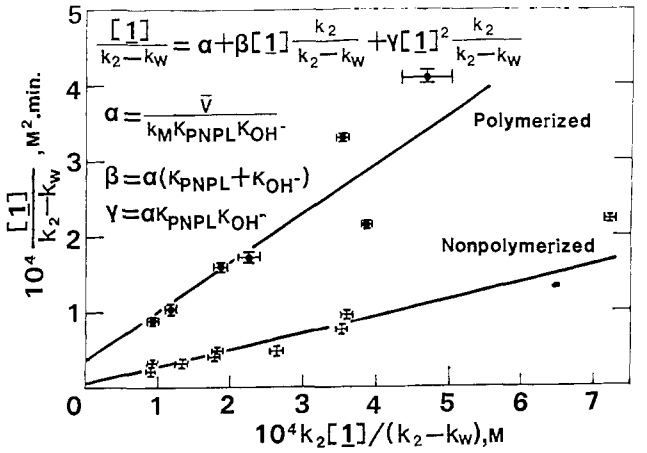

Figure 4. Kinetic treatment of PNA hydrolyses in **1** vesicles according to eq 9.

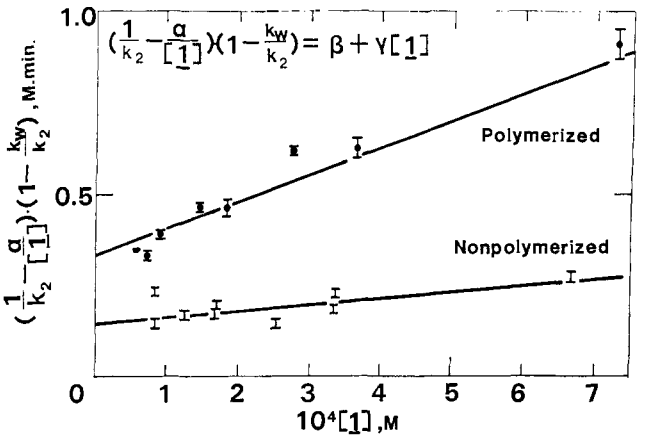

Figure 5. Kinetic treatment of PNPA hydrolyses in **1** vesicles according to eq 13.

the observed second-order rate consant for the hydrolysis of PNPL in the presence of vesicles, k_2, is expressed by[7,27,28]

$$k_2 = \frac{(k_M/\bar{V})K_{PNPL}K_{OH^-}[\mathbf{1}] + k_w}{(1 + K_{PNPL}[\mathbf{1}]\bar{V})(1 + k_{OH^-}[\mathbf{1}])} \quad (8)$$

where K_{PNPL} and K_{OH^-} are the binding constants for the interaction of PNPL and OH^- with the vesicles. The experimental data on the dependence of k_2 on vesicle concentrations (Table III) can be used to calculate K_{PNPL}, K_{OH^-}, and $k_M/\bar{V}$, in a manner analogous to that utilized for micelle-catalyzed reactions.[29-31] For this purpose, eq 8 is transformed to

$$\frac{[\mathbf{1}]}{k_2 - k_w} = \alpha + \beta[\mathbf{1}]\frac{k_2}{k_2 - k_w} + \gamma[\mathbf{1}]^2\frac{k_2}{k_2 - k_w} \quad (9)$$

where

$$\alpha = \bar{V}/k_M K_{PNPL}K_{OH^-} \quad (10)$$

$$\beta = (K_{PNPL} + K_{OH^-}) \quad (11)$$

$$\gamma = \alpha K_{PNPL}K_{OH^-} \quad (12)$$

Plots of the data for the hydrolysis of PNPL in nonpolymerized **1** and polymerized **1** vesicles according to eq 9 are given in Figure 4. Using values of the intercepts in Figure 4 (α values) allows further analysis in terms of rearranged eq 9

$$\left(\frac{1}{k_2} - \frac{\alpha}{[\mathbf{1}]}\right) - \left(1 - \frac{k_w}{k_2}\right) = \beta + \gamma[\mathbf{1}] \quad (13)$$

Plots of the data according to eq 13 are shown in Figure 5. Values for β and γ were obtained from the intercepts and slopes, which in turn allowed the assessments of $K_{PNPL} = 1.3 \times 10^4$ M^{-1} and $K_{OH^-} = 1.8 \times 10^3$ M^{-1} in nonpolymerized **1** vesicles and $K_{PNPL} = 5.4 \times 10^3$ M^{-1} and $K_{OH^-} = 3.6 \times 10^3$ M^{-1} for polymerized **1** vesicles. These values are in excellent agreement with those determined independently from solubility ($K_{PNPL} = 1.1 \times 10^4$ and 4.8×10^3 M^{-1} for nonpolymerized **1** and polymerized **1** vesicles) and pH measurements ($K_{OH^-} = 2.7 \times 10^3$ and 2.4×10^3 M^{-1} for nonpolymerized **1** and polymerized **1** vesicles, Table II) and lend further credence, therefore, to the assumptions used in deriving eq 8. The best fit of the data were obtained on using $k_M/\bar{V}$ values of 5.4×10^{-3} and 1.3×10^{-3} min^{-1} for the nonpolymerized **1** and polymerized **1** vesicles. Assuming $\bar{V}$ to be 0.5 M^{-1} for surfactant vesicles[28] leads to substantial apparent reduction of the hydrolysis rate in the environment of the vesicles.

Data are rationalized in terms of complete distribution of both PNPL and OH^- in both sides of the vesicles at a time scale faster than the hydrolysis. Apparently polymerization of styrene in the matrix of **1** vesicles does not affect this situation. This is in accord with our proposed patch type polymerization[17] and hydroxide ion permeabilities.[32]

Aminolysis of PNPL. Addition of EDA to both nonpolymerized and polymerized **1** vesicles containing PNPL resulted in the biphasic liberation of *p*-nitrophenolate which could be resolved into a faster (governed by k_{fast}) and a slower (governed by k_{slow}) process (Figure 2 and Table IV). Kinetic rate profiles of both k_{fast} and k_{slow} as functions of **1** concentrations were analogus to those observed for PNPL hydrolysis. The complexity of aminolysis in the presence of vesicles did not warrant the quantitative treatment of the data in terms of eq 9. Extrapolations of the logarithmic decays of the fast and slow components to zero times indicated that 59 ± 5% of PNPL decayed by the fast process and 41 ± 5% decayed by the slow process. The observed monodispersity (see Results) excludes the possibility that k_{fast} and k_{slow} originate in two distinct sets of vesicle populations. The method of PNPL introduction does not influence the kinetics of aminolysis. Identical k_{fast} and k_{slow} values were obtained for runs in which PNPL was co-sonicated with **1** and in which PNPL was added to already formed vesicles.[33] Apparently, PNPL is rapidly distributed in the vesicles. Amphiphatic compounds are known to distribute rapidly in vesicles.[34] The appreciable binding of EDA coupled with its very much slower reactivity with PNPA in water[35] confirm the vesicles to be the site of aminolysis. Although it may be tempting to assign k_{fast} and k_{slow} to extravesicular and endovesicular reactivities,[24] the availability data are insufficient for this assignment. k_{slow} may well be due to the rate-limiting diffusion of EDA to a site where PNPL is buried.

Consideration of PNPL aminolysis in nonpolymerized and polymerized vesicles reveals additional complexities. The most striking result is the prevalence of biphasic kinetics in polymerized **1** vesicles even though only 50% of *p*-nitrophenyl laurate is liberated (Table V). It implies that there are at least three different sites for the aminolysis. One site, corresponding to ca. 50% of the reaction, becomes unavailable for the EDA attack upon polymerization. Most likely, this site is the inner surface of vesicles and corresponds to endovesicular reactivity. Since k_{fast} is some 30-fold slower in polymerized **1** than nonpolymerized **1** vesicles (Table V) and since the partitioning of EDA is not altered upon vesicle polymerization (see Results), PNPL distributes itself differently in polymerized and nonpolymerized vesicles. Some of the PNPL is "buried" to a greater extent than others. This

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gives rise to k_{slow} in polymerized **1** vesicles. A similar situation has been encountered in the dithionite ion cleavage of 5,5'-dithiobis(2-nitrobenzoic acid), Ellman's reagent, in dihexadecyldimethylammonium vesicles.[26] The relative contributions of the fast and slow components of the reaction varied as a function of time elapsed (46 ms to 1-5 s) between the addition of the Ellman's reagent and the dithionite ion. These results were rationalized in terms of the time required for distribution of the substrate between the vesicle surface (k_{fast}) and substrate (k_{slow}).[26]

Observation of the three reaction sites in polymerized **1** vesicles does not imply an identical behavior in nonpolymerized vesicles. Clearly, reactivities in vesicles and polymerized vesicles are complex and their understanding presents a worthy challenge.

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Structural Characterization of Gas-Phase Complexes of Alkanes, Alkenes, and Carbon Monoxide with the Atomic Iron Ion

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Abstract: Gas-phase clusters of Fe^+ with hydrocarbons and carbon monoxide are characterized by collision-induced decomposition (CID) mass spectrometry. The clusters are formed in ion-molecule reactions of $Fe(CO)_n^+$ ions with hydrocarbons and ketones. Two different $FeC_4H_{10}^+$ species are characterized. $FeC_3H_8^+$, $FeC_2H_6^+$, and $FeCH_4^+$ species are observed and characterized. Oxidative addition of C-C and C-H bonds to the metal occurs in these complexes. Four different $FeC_4H_8^+$ species are characterized. $FeC_4H_6^+$ formed in four different reactions are all found to have the same structures, a metal-1,3-butadiene complex. $FeC_3H_6^+$ and $FeC_2H_4^+$ species formed in several different reactions are found to be metal-olefin complexes. Four different species of stoichiometry $FeCOC_4H_{10}^+$ are observed. Evidence of $FeCO^+$ insertion into C-C and C-H bonds in these species is described. Two different $FeCOC_2H_6^+$ species are observed. Two different FeH_2CO^+ species are observed, one of which has the hydrogen atoms bound to the metal. Evidence is presented that addition of C-H bonds to the metal occurs in $Fe_2(CO)_4C_4H_{10}^+$ clusters. Correlation is observed between the CID spectra of several ions and the exothermicity of the reactions in which they are formed. Product distributions for reaction between butanes and Fe^+ formed by 70-eV electron impact on $Fe(CO)_5$ matches product distributions obtained for Fe^+ formed in other ways. It is deduced from the CID spectrum of one isomer of $FeCOC_2H_6^+$ that $IP(FeCH_3) \approx IP(CH_3CO)$, which implies $D(Fe-CH_3) \approx 42$ kcal/mol.

The first examples of oxidative addition of alkane carbon-carbon bonds to transition metals have recently been reported.[1-3] Evaporated clusters of Ni atoms[1] and Zr atoms,[2] for example, when condensed with alkanes react to form smaller alkanes. The group 8 first-row atomic ions react in the gas phase with alkanes to form smaller alkanes and metal-olefin complexes.[3,4] The discovery of gas-phase oxidative addition processes involving carbon-carbon bonds provides a unique opportunity to study the dynamics of oxidative addition. Important thermochemical and mechanistic information on the formation of metal to carbon bonds has been obtained in several such studies.[3-14]

We recently described the formation of complexes of alkanes with atomic transition-metal ions.[4] The complexes result from ion-molecule reactions in metal carbonyls and are stable in the gas phase. These complexes might be considered the simplest case of an alkane absorbed on a metal surface. The initial communication described the structural characterization of complexes of Fe^+ with the C_4H_{10} isomers using the techniques of collision-induced-dissociation mass spectrometry.[4] The present report describes more complete characterization of complexes of Fe^+ with 2-methylpropane and butane as well as characterization of Fe^+ complexes with propane, ethane, and methane. Metal-olefin complexes formed in the reactions of Fe^+ with the alkanes are also characterized.

The effects of adding a CO ligand to a metal-alkane complex are probed by examining the collision-induced decomposition spectra of $FeCO(C_4H_{10})^+$, $FeCO(C_2H_6)^+$, and FeH_2CO^+ ions prepared in several ways. Ions of the $Fe_2(CO)_4(C_4H_{10})^+$ stoichiometry are structurally examined to probe the effect of an additional Fe atom in the cluster.

Experimental Section

The collision-induced decomposition experiments were performed on a three-sector mass spectrometer at the Midwest Center for Mass Spectrometry. The instrument, described in detail elsewhere,[15] is a

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