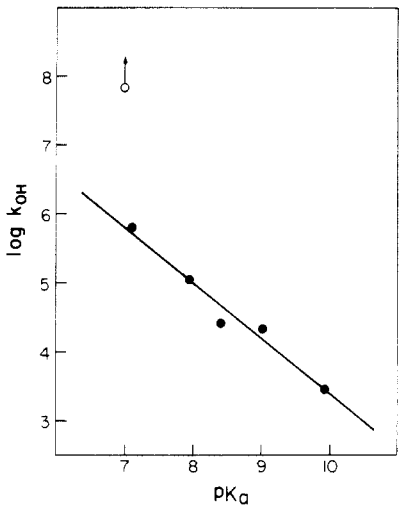
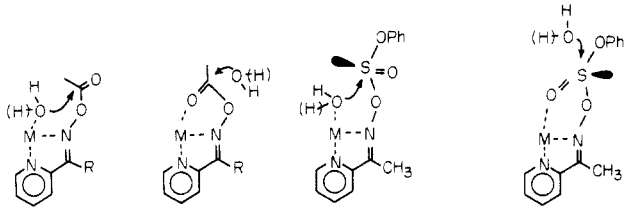


Figure 2. The plot of log k_{OH} (●) against pK_a of leaving phenol for the alkaline hydrolysis of aryl phenyl sulfite (ArOSOOPh) esters. The unit of k_{OH} is M^{-1} s^{-1}. The aryl groups employed are *p*-NO_2, *p*-CN, *m*-NO_2, *m*-Cl, and unsubstituted phenyls (in the order of increasing pK_a values). The data point for Zn(II)–**2** (○) represents the lowest limit as discussed in the text. The pK_a of the leaving group of Zn(II)–**2**, i.e., the Zn(II) complex of 2-acetylpyridine oxime, is 7.0.[1c]

therefore, can be taken to indicate that additional catalytic factors are needed to explain the fast rate for Zn(II)–**2**.[12]

In the case of the acetyl esters, extra catalytic roles were also needed in addition to the decrease in the pK_a of leaving oxime in order to explain the observed rate data.[1a,b] The catalytic factors involved in B (nucleophilic attack by the metal bound water molecule or hydroxide ion) or C (polarization of the carbonyl group) were proposed,[1a] and the detailed analysis of kinetic data chose B as the correct mechanism.[1b,c] For the sulfite ester, D and E contain the extra catalytic roles proposed in B and C, respectively. In



the hydrolysis of sulfite esters, both the entering and the leaving groups should occupy apical positions in trigonal bipyramidal intermediates or transition states. This is not possible in the mechanism of D. Therefore, the mechanism of E, which assumes both an increase in the leaving ability of the oxime anion and the polarization of the sulfinyl group, is the most probable mechanism for the Zn(II)-catalyzed hydrolysis of **2**.

It is noteworthy that two five-membered chelate rings (E) are formed in the case of the Zn(II) complex of sulfite ester **2**, while only one chelate ring (B) is formed in that of the corresponding acetyl esters. In the metal ion catalyzed hydrolysis of other esters in which coordination of the carbonyl oxygen atoms to metal ions is facilitated, the metal ion catalysis can proceed through mechanisms analogous to C.[1h,2] Therefore, it appears that the mechanism of C does not operate because of the strain involved in the chelate rings.[1h] The formation of the two-chelate-ring system (E) in the Zn(II)–**2** complex in contrast to B can be attributed to the differences in the bond lengths and bond angles between the sulfite and acetyl esters. Thus, the longer bond lengths of sulfur–oxygen double and single bonds compared with carbon–oxygen double and single bonds can relieve the ring strain. In addition, the configuration of sulfur in sulfite esters is tetrahedral, while that of carbonyl carbon of acetyl esters is trigonal. On the other hand, the sulfinyl sulfur becomes trigonal bipyramidal and the carbonyl carbon tetrahedral in transition states. The consequent differences in bond angles around these atoms may also contribute to the relief of the ring strain.

Acknowledgment. This work was supported by a grant from Korea Science and Engineering Foundation.

Registry No. **2**, 108711-91-7; Zn^{II}, 23713-49-7.

Supplementary Material Available: Derivation of eq 1 (2 pages). Ordering information is given on any current masthead page.

(12) The catalytic effect of the decrease in the pK_a of the leaving oxime caused by metal complexation is best estimated by using the linear plot of log k_{OH} against pK_a of oximes for various oxime phenyl sulfite esters. For this purpose, the oxime anions of the sulfite esters should have greater leaving ability than phenolate ion. Such oxime phenyl sulfite esters, however, are not readily accessible. On the other hand, the high efficiency of the Zn(II) catalysis in the sulfite ester hydrolysis may be emphasized by k_{cat}^{OH} (the bimolecular rate constant for the attack of OH^- at MS) which is much greater than k_{OH}' (the bimolecular rate constant for the attack of OH^- at SH^+).

The Induced Decomposition of *S*-*tert*-Butyl Benzenethioseleninate[1a]

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Thiols react with benzeneseleninic acid ($PhSeO_2H$) with the overall stoichiometry shown in eq 1.[2] The reaction

$$3RSH + PhSeO_2H \rightarrow RSSePh + RSSR + 2H_2O \quad (1)$$

takes place in several steps (eq 2a–c), the first (eq 2a) being reaction of the seleninic acid with the thiol to form a thioseleninate, PhSe(O)SR (**1**).[2] When R = *n*-Bu reaction of PhSe(O)SBu-*n* (**1a**) with thiol (eq 2b) is faster than its formation. However, when R = *t*-Bu, eq 2b is much slower

$$PhSeO_2H + RSH \rightarrow PhSe(O)SR + H_2O \quad (2a)$$
$$\textbf{1a}, R = n\text{-Bu}$$
$$\textbf{1b}, R = t\text{-Bu}$$

$$PhSe(O)SR + RSH \rightarrow RSSR + PhSeOH \quad (2b)$$

$$PhSeOH + RSH \rightarrow PhSeSR + H_2O \quad (2c)$$

than eq 2a, especially in weakly acid solution. As a consequence, when $PhSeO_2H$ was allowed to react with an approximately equimolar amount of *t*-BuSH in aqueous dioxane Kice and Lee[2] were able to isolate the first known example of a thioseleninate, PhSe(O)SBu-*t* (**1b**). Isolation of a thioseleninate and investigation of its chemistry was of particular interest because of the suggestion[3] that an Se(O)S functionality may be an intermediate in the reaction cycle for the important enzyme glutathione peroxidase.

(1) (a) This research was supported by the National Science Foundation (Grant CHE-82-15140). (b) Present address: Department of Chemistry, University of Denver, Denver CO 80208.
(2) Kice, J. L.; Lee, T. W. S. *J. Am. Chem. Soc.* **1978**, *100*, 5094.
(3) Ganther, H. E. *Chem. Scr.* **1975**, *8A*, 79.

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As obtained by Kice and Lee thioseleninate **1b** was stable in dilute ($\sim 10^{-4}$ M) solution in aqueous dioxane but underwent quite rapid decomposition at room temperature in relatively concentrated ($\sim$0.5 M) solution in acetone-d_6. Identified products of this decomposition were *t*-BuSSBu-*t*, PhSeSBu-*t*, and PhSeSePh.

The facile decomposition of **1b** at room temperature in acetone solution was both surprising and unexpected. The objective of the present study was to explore the decomposition in detail with the aim of determining its mechanism and the reason for the singular instability of the thioseleninate. As we will see, this further examination has shown that **1b** itself is thermally quite stable at room temperature in acetone solution. The marked instability of the **1b** isolated by Kice and Lee is due to the presence of small concentrations of an impurity which is able to induce rapid decomposition of the thioseleninate.

Results and Discussion

S-tert-Butyl benzenethioseleninate (**1b**) was prepared by the same procedure employed previously,[2] i.e., reaction of benzeneseleninic acid ($PhSeO_2H$) with a slight molar excess of *t*-BuSH in aqueous dioxane until the ultraviolet spectrum of the solution indicated the concentration of **1b** (λ_{max} 265 nm) had reached a maximum, followed by removal of the solvent and excess thiol by lyophilization of the frozen reaction solution. In acetone-d_6 the protons of the *tert*-butyl group of **1b** appear in ^{1}H NMR as a singlet at δ 1.63. As **1b** decomposes this signal disappears and is replaced by a singlet at δ 1.32 due to the *t*-Bu groups of two of the decomposition products, *t*-BuSSBu-*t* and *t*-BuSSePh. Previously[2] enough **1b** always underwent decomposition during workup so that the ^{1}H NMR of the isolated **1b** contained a singlet at δ 1.32 with an integrated intensity equal to at least $^1/_{10}$ that of the singlet at δ 1.63. In the present work more care in the lyophilization (see Experimental Section) allowed purer samples of **1b** to be prepared in which the intensity of the δ 1.32 singlet was always *less than* $^1/_{25}$ that of the singlet at δ 1.63.

The rate of decomposition of **1b** (0.08–0.17 M) in acetone-d_6 was followed by monitoring the disappearance of the singlet at δ 1.63. Initial studies, done with **1b** prepared from commercial benzeneseleninic acid (Aldrich Chemical, 99%, mp 120–121 °C), showed the same type of rapid disappearance of **1b** at room temperature noted earlier by Kice and Lee.[2] First-order plots (log [**1b**] vs. time) for the decomposition exhibited downward curvature (acceleration in rate of disappearance of **1b**) as the reaction proceeded. A higher initial concentration of **1b** also resulted in a faster rate of decomposition. On the other hand, samples of **1b** prepared from benzeneseleninic acid that had been further purified (mp 122–123 °C) by two recrystallizations from water *did not decompose* to any significant extent in acetone-d_6 over the same period. This shows that, contrary to previous[2] suggestion, **1b** itself is not per se thermally unstable at room temperature in acetone solution. The rapid decomposition Kice and Lee[2] observed is due to the decomposition of **1b** being induced by some impurity present in low concentration in both the **1b** they isolated and in the ester prepared in the present work from $PhSeO_2H$ that had not been further purified by several additional recrystallizations.

Insight into the probable nature of the impurity responsible for inducing the decomposition of **1b** was provided by a series of experiments that examined the effect of various compounds on the stability of solutions of "stable" **1b**. Neither diphenyl diselenide (PhSeSePh) nor benzeneseleninic anhydride (PhSe(O)OSe(O)Ph) taken separately had any effect, but when a 2:1 molar mixture of the diselenide and the seleninic anhydride was heated in acetonitrile-d_3 and then added to a 0.16 M solution of **1b** in acetone-d_6, decomposition of the thioseleninate occurred quite rapidly and in the same manner kinetically as in the experiments with "unstable" **1b**. The same effect could also be produced by adding a solution prepared by oxidation of PhSeSePh with 1 molar equiv of *m*-chloroperoxybenzoic acid (MCPBA).

Reaction of diphenyl diselenide with benzeneseleninic anhydride is known[4] to generate an equilibrium amount of benzeneselenenic anhydride (eq 3). On the basis of the

$$2PhSeSePh + PhSe(O)OSe(O)Ph \rightleftarrows 3PhSeOSePh \quad (3)$$

behavior of bis(*p*-fluorophenyl) diselenide,[5] oxidation of PhSeSePh with 1 mol of MCPBA would also be expected to give PhSeOSePh, in equilibrium with diphenyl diselenide and benzeneseleninic anhydride (eq 4).

$$PhSeSePh \xrightarrow{1\ mol\ of\ MCPBA} PhSeOSePh \rightleftarrows {}^2/_3PhSeSePh + {}^1/_3PhSe(O)OSe(O)Ph \quad (4)$$

The above experiments indicate that the impurity responsible for the facile induced decomposition of **1b** is apparently benzeneselenenic anhydride (PhSeOSePh, **2**). That the anhydride is needed and the selenenic acid (PhSeOH) itself is ineffective is suggested by the fact that if the solution from reaction of PhSeSePh with PhSe(O)OSe(O)Ph was treated with water to hydrolyze the various selenium acid anhydrides before being added to the solution of **1b** rapid decomposition of the thioseleninate did not occur.

Since the amount of **2** present in samples of "unstable" **1b** is almost certainly extremely small, the induced decomposition of **1b** by **2** is presumably some type of chain process. The downward curvature in plots of log [**1b**] vs. time for the decomposition suggests that the concentration of the selenenic anhydride probably increases as the decomposition progresses; i.e., the reaction produces more **2** as a product than is consumed in initiating the chain decomposition.[6]

Kice and Lee[2] established that *tert*-butyl disulfide, diphenyl diselenide, and *tert*-butyl benzeneselenenyl sulfide (PhSeSBu-*t*) were products of the decomposition of **1b** but did not determine the fate of the oxygen atom in the thioseleninate. On the basis of the report by Woodbridge[7] that O_2 was a major product of the thermal decomposition of dodecaneseleninic anhydride, $C_{12}H_{25}Se(O)OSe(O)C_{12}H_{25}$, they speculated that O_2 might also be a major product of the decomposition of **1b**. This has been shown in the present study *not* to be the case. A carefully degassed solution of "unstable" **1b** was allowed to decompose in a sealed system under nitrogen. At the end of the decomposition O_2 could not be detected in the atmosphere above the solution. Extraction of the product residue remaining after removal of the solvent with aqueous sodium carbonate led to the isolation of considerable (0.35 mol/mol of **1b**) of benzeneseleninic acid, indicating that either $PhSeO_2H$ or its anhydride, PhSe(O)OSe(O)Ph, is an important oxygen-containing product of the decomposition of **1b**. This same product study gave the following yields (mol/mol **1b**) of the three non-oxygen-containing com-

(4) (a) Hori, T.; Sharpless, K. B. *J. Org. Chem.* **1978**, *43*, 1689. (b) Reich, H. J.; Wollowitz, S.; Trend, J. E.; Chow, F.; Wendelborn, D. F. *Ibid.* **1978**, *43*, 1697.

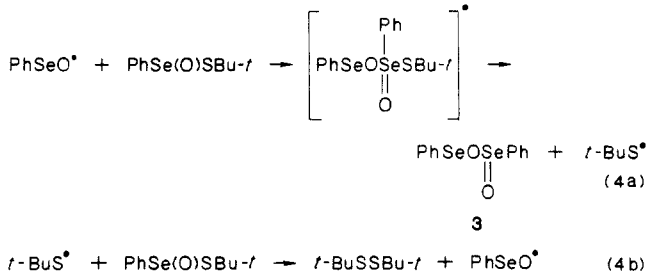
(5) Gancarz, R. A.; Kice, J. L. *Tetrahedron Lett.* **1981**, 1661.

(6) Significant decomposition of **1b** during workup (resulting in formation of some **2**) is probably the explanation for the instability of the **1b** isolated by Kice and Lee,[2] since the benzeneseleninic acid that they used for the synthesis had been recrystallized from water after being prepared.

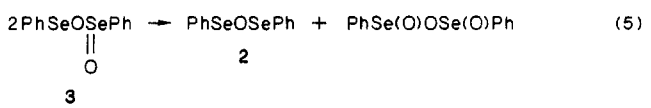
(7) Woodbridge, D. T. *J. Chem. Soc. B* **1966**, 50.

pounds identified previously[2] as decomposition products: *t*-BuSSBu-*t*, 0.47; PhSeSePh, 0.27; PhSeSBu-*t*, 0.05.

Brief speculation regarding the exact nature of the chain reaction responsible for the decomposition of **1b** seems in order. Although an ionic mechanism for the chain reaction cannot be ruled out, a mechanism with free radical intermediates is probably more likely. A radical chain that can account for the principal reaction products is shown in eq 4a,b. The mixed selenenic–seleninic anhydride (**3**)



could disproportionate in the manner shown in eq 5, with the selenenic anhydride (**2**) so formed equilibrating with diselenide and seleninic anhydride as outlined in eq 3.



Generation of PhSeO• radicals to initiate the chain could come from both homolytic dissociation of 2 (eq 6a) and reaction of the PhSe• radicals also produced in that dissociation with **1b** (eq 6b). Since the initiator of the chain

$$\text{PhSeOSePh} \rightarrow \text{PhSe}\cdot + \text{PhSeO}\cdot \quad (6a)$$

$$\text{PhSe}\cdot + \text{PhSe(O)SBu-}t \rightarrow \text{PhSeSBu-}t + \text{PhSeO}\cdot \quad (6b)$$

reaction, **2**, is also produced as one of the products (eq 5) the increase in rate with increasing extent of decomposition in the curved kinetic plots can be accounted for.

Alternatives to the reaction scheme above can, of course, be suggested, but in the interest of brevity will not be outlined. The key point emerging from the present study is that, contrary to what was believed by Kice and Lee,[2] **1b** per se is not thermally unstable at room temperature. Its facile decomposition under those conditions is the result of a chain reaction that requires benzeneselenenic anhydride (**2**) for its initiation.

Experimental Section

Preparation and Purification of Materials. 2-Methyl-2-propanethiol (Aldrich) was purified by fractional distillation (bp 64–65 °C) and stored under nitrogen. Benzeneseleninic anhydride (Aldrich) was dried under vacuum in a desiccator containing phosphorus pentoxide and then stored in a sealed vial in the same desiccator until used. Diphenyl diselenide (Aldrich) was recrystallized twice from hexane. Benzeneseleninic acid (Aldrich) was used both without further purification (mp 120–121 °C) and after being recrystallized twice from water (mp 122–123 °C). Dioxane was purified in the manner outlined by Fieser and Fieser.[8] The deuteriated solvents (Aldrich) used in the NMR studies were of the highest purity commercially available.

S-tert-Butyl benzenethioseleninate (**1b**) was prepared from *t*-BuSH and benzeneseleninic acid in the manner outlined by Kice and Lee[2] with the modification that during the latter stages of the lyophilization procedure the flask containing the **1b** was cooled in a carbon tetrachloride slush bath (−23 °C) rather than in an ice bath (0 °C). This modification reduced decomposition of **1b** during workup essentially to zero. This was shown by the fact that the intensity of the singlet at δ 1.32 due to decomposition products (PhSeSBu-*t* and *t*-BuSSBu-*t*) of **1b** in the isolated thioseleninate was always less than $^1/_{25}$ of the intensity of the signal at δ 1.63 for the protons in the *t*-Bu group of **1b**. In contrast, the earlier[2] lyophilization procedure invariably gave **1b** where the singlet at δ 1.32 was *at least* $^1/_{10}$ the intensity of the singlet at δ 1.63.

Prior to freezing and lyophilization the reaction solution was subdivided in most cases into a number of portions of volumes such that each would yield, after removal of the solvent, an amount of **1b** appropriate for a single NMR kinetic run. Each portion was placed in a separate tared flask, and after lyophilization was complete, the tightly sealed flask was stored at dry ice temperature until used. When stored in this manner samples of **1b** were stable indefinitely.

Kinetics of the Decomposition of 1b. At −20 °C a measured volume of acetone-d_6 (2.0–3.0 mL) was added to a sample of **1b** (0.40–1.0 mmol) prepared as described above. Once solution was effected, sufficient additional acetone-d_6 (containing 1% Me_4Si) to give the desired initial concentration of **1b** was added, and a portion of the solution was transferred to an NMR tube and placed in a Varian XL-100-15 NMR spectrometer, whose probe temperature was thermostated at 22.0 ± 1.0 °C.

As noted earlier, the protons of the *t*-Bu group of **1b** give rise in the NMR to a sharp singlet at δ 1.63. In the products of the decomposition of **1b** these same protons appear as a singlet at δ 1.32. These two peaks and the peak for Me_4Si were integrated at selected times after the initiation of the experiment. The ratio of the intensity of the singlet at δ 1.63 to the intensity of the signal for Me_4Si was measured vs. time to monitor the disappearance of **1b**. The disappearance of the signal at δ 1.63 was accompanied by a concomitant increase of the correct magnitude in the intensity of the signal at δ 1.32.

In those runs in which the effect of various additives on the disappearance of **1b** was investigated 0.5 mL of a solution containing the proper amount of **1b** in acetone-d_6 was mixed with 0.5 mL of a solution containing the additive, the resulting solution was transferred to an NMR tube, and the integrated intensity of the signal at δ 1.63 was measured as a function of time in the fashion outlined above. The solvents for the solutions of the additives were (additive, solvent): diphenyl diselenide, acetone-d_6; benzeneseleninic anhydride, acetonitrile-d_3; **2** (from reaction of PhSeSePh and PhSe(O)OSe(O)Ph), acetonitrile-d_3; **2** (from oxidation of PhSeSePh with 1 mol of MCPBA), $CDCl_3$.

Solutions containing **2** were prepared in two different ways. (a) Benzeneseleninic anhydride (0.018 g, 0.05 mmol) was dissolved in 2.0 mL of anhydrous acetonitrile-d_3 and placed in a 10 mL round-bottom flask fitted with a reflux condenser topped by a drying tube. Diphenyl diselenide (0.031 g, 0.10 mmol) was added and the resulting mixture was refluxed gently for 12–15 h to ensure the establishment of the equilibrium shown in eq 3. (b) Diphenyl diselenide (0.15 g, 0.5 mmol) was dissolved in chloroform-*d* (1.0 mL). To this was added dropwise, 0.50 mmol of *m*-chloroperoxybenzoic acid in 1.0 mL of $CDCl_3$. Once addition was complete the reaction mixture was stirred for 5–10 min at room temperature, filtered, and then used promptly.

In one run using a solution containing **2** generated by equilibration of PhSeSePh and PhSe(O)OSe(O)Ph (method a) 0.1 mL of D_2O was added to a final solution, which was then allowed to stand overnight before being used in an NMR experiment with **1b**.

Search for Evolution of Oxygen during Decomposition of 1b. A sample of **1b** (0.8 mmol) prepared from unrecrystallized benzeneseleninic acid was dissolved in 3.0 mL of acetone. The solution was placed in a two-necked vessel, one neck of which was fitted with a vacuum-tight rubber septum and the other of which was fitted with an ℸ joint for attachment to a vacuum line. The flask was attached to the vacuum line, and the solution was degassed by using standard procedures. After degassing was complete oxygen-free dry nitrogen was admitted to the flask, the neck attached to the vacuum line was flame-sealed, and the flask was removed from the vacuum line. The flask was then allowed to stand at room temperature until decomposition of **1b** was complete. At that time a gas-tight syringe was inserted through the septum and used to withdraw a sample of the atmosphere in the flask above the reaction solution. This gas sample was

(8) Fieser, L. F.; Fieser, M. F. *Reagents for Organic Synthesis*; Wiley: New York, 1967; p 333.

injected into a Gow-Mac Series 550 gas chromatograph fitted in series with an 8 ft molecular sieves column followed by a 6 ft Poropak N column. This particular configuration is designed for the separation and identification of atmospheric gases. The chromatogram showed no indication of the presence of any O_2 in the gas sample.

Products of the Decomposition of 1b. Thioseleninate **1b** (2.0 mmol) prepared from unrecrystallized benzeneseleninic acid was dissolved in 10 mL of acetone and allowed to stand at room temperature until decomposition was complete. The acetone was then removed under reduced pressure, and the residue was dissolved in chloroform and extracted several times with aqueous sodium carbonate. The chloroform solution was dried (Na_2SO_4), the solvent removed, and the residue chromatographed on silica gel with hexane as eluent. The chromatography yielded *tert*-butyl disulfide (0.92 mmol), diphenyl diselenide (0.54 mmol), and a small amount of *tert*-butyl benzeneselenenyl sulfide (0.05 mmol), each identical with known samples[2] of these compounds.

The aqueous extracts were concentrated in volume and then carefully acidified with 6 N sulfuric acid. The benzeneseleninic acid (0.70 mmol, mp 122–123 °C) that crystallized out after acidification was filtered off and its identity further confirmed by comparison of its infrared spectrum (KBr) with that of the known sample of this acid mentioned in the paragraph dealing with preparation and purification of materials.

Registry No. **1b**, 67680-11-9; *t*-BuSSBu-*t*, 110-06-5; PhSeSePh, 1666-13-3; PhSeSBu-*t*, 67680-10-8; $PhSeO_2H$, 6996-92-5.

Two New Amphiphilic Catalysts for Ester Hydrolysis

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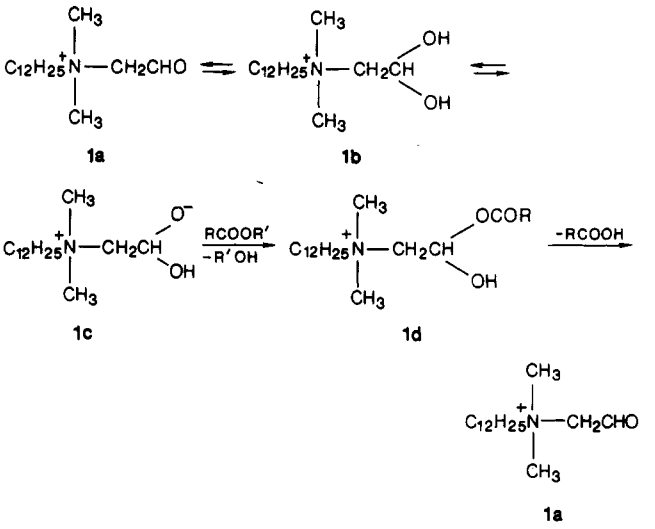
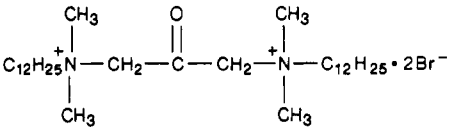
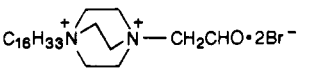
In 1985 we reported a functionalized surfactant (**1a**) capable of catalyzing the hydrolysis of carboxylic and phosphate esters.[1] Although many examples of functionalized surfactants have been published,[2-12] few exhibit true turnover behavior[1,11] as does **1a**. Thus, under mildly basic conditions **1a** hydrates to **1b**, acylates to **1d**, and then ejects the carboxyl to reform the original catalyst **1a**. Rate accelerations with *p*-nitrophenyl diphenyl phosphate were found to be a substantial (but hardly enzyme-like) 1800-fold. In this paper, we examine the esterolytic activity of two new systems, **2** and **3**, which could, it was initially



hoped, manifest even greater catalytic accelerations. Since **2** and **3** are dicationic, the pK_a of their hydrates should



2



3

be less than the 10.9 observed for **1b**. Consequently, formation of the nucleophilic oxyanion would be favored under the physiological conditions where we wished to operate.

Surface tension measurements on **2** revealed a critical micelle concentration of 4.3×10^{-4} M (half that of **1**). Hydration behavior, on the other hand, differs markedly between **1** and **2**. Whereas **1** is totally hydrated in water at all pH values, **2** requires pH 10 (borate buffer) for the ^{13}C NMR peak of the carbonyl (194 ppm) to disappear. A mixture of ketone, hydrate, and enolate was observed for **2** at pH 9, and at neutrality only traces of hydrate (with its characteristic hydrate carbon signal at 80 ppm) are present. Apparently, banking the carbonyl of **2** with two electronegative quaternary ammonium groups is not sufficient to overcome the general preference for hydration that aldehydes have over ketones.[13]

The catalytic ability of **2** toward *p*-nitrophenyl hexanoate was disappointing. Thus, 2.0 mM **2** at pH 8.0 and 25.0 °C gave a $k_{obsd} = 6.5 \times 10^{-5}$ s^{-1} which is only 8-fold larger than in the absence of **2**. Elevating the pH to 10.0, in order to increase the concentration of hydrate, led to a $k_{obsd} = 1.4 \times 10^{-3}$ s^{-1}, which is only 2-fold greater than background. It seems clear that both hydration equilibria and acyl-transfer rates are adversely affected by steric affects, and hence we investigated **3** where (a) the aldehyde functionality is maintained and (b) the ammonium group proximate to the reactive center is tied back in the bicyclic ring system, thereby minimizing steric problems.

Compound **3** has a critical micelle concentration, determined tensiometrically, of 2.0×10^{-3} M. This high value for a hexadecyl surfactant no doubt reflects electrostic repulsions involved when two cationic charges *per chain* are forced to reside at the micelle surface. As expected,

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