reaction), $Fe(CO)_3$diars[28] (protonation, no further reaction), $HRe(CO)_5$[29] (quantitative formation of $ClRe(CO)_5$). Clearly, further studies are necessary to determine the scope and limitations of this new procedure for polyhydride synthesis.

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(6) Undoubtedly, *tert*-butyl chloride slowly hydrolyzes under these conditions to give aqueous HCl which then eventually provides **1**. In support of this interpretation, we find that **2** does not react with *tert*-butyl chloride in the absence of water.
(7) Phosgene from the reaction of anhydrous HCl with **2** or **3** in THF was isolated in the form of urea. For example, anhydrous HCl was bubbled (via all-glass tubing) through a solution of 2.00 g of **1** in 50 ml of THF. The solution rapidly changed colors from red to yellow to red. With the HCl flow stopped, the solution was stirred for 1 h and then all volatiles were removed (leaving after recrystallization) (vide supra) 1.1 g (75%) of **1**) and trapped out in a flask containing 50 ml of anhydrous ammonia. After stirring the ammonia solution for 1 h at −50 °C, all volatiles were again removed, leaving a colorless mixture of ammonium chloride and urea. Neutralization of an aqueous solution of this mixture with sodium hydroxide, followed by evaporation, left NaCl and urea which were cleanly separated by treatment with absolute ethanol. Evaporation of ethanol left 0.14 g (64% yield) of substance identical with genuine urea.
(8) No direct evidence for the formation of the bracketed intermediates has been obtained; however, clearly protonation of **3** followed by halide attack of coordinated carbon monoxide are required steps in the actual process. In the presence of water the C(OH)X grouping is likely to be hydrolyzed to a carboxyl group (vide infra). Also, as suggested by a referee, a second halide attack of the hydroxyhalocarbene may precede the protonation process.
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(13) The only other neutral complexes containing three terminal carbonyl groups which also absorb in this region are M(dien)$(CO)_3$ (M = Cr, Mo, and W). For example, for M = Mo, $\nu$(CO) are 1898 and 1758 $cm^{-1}$ (C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, **2**, 533 (1963)).
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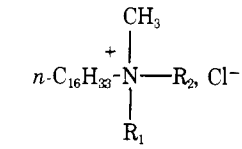
## Sequential Bifunctional Micellar Catalysis

*Sir:*

The comparison of micelles and enzymes is now commonplace,[1] but the rational design of functionalized surfactants to provide increasingly exact enzyme analogues is a more recent venture.[2] A key feature of chymotrypsin catalysis is basic activation by an imidazole group (His-57) of the Ser-195 hydroxyl moiety; the latter's oxygen is the nucleophile which attacks the substrate's carbonyl group.[3] Many "model enzymes" have been designed to mimic this mechanism.[4] Micellar chymotrypsin models have included hydroxyl-[5] and imidazole-functionalized[6] surfactants, but few studies of *bifunctional* micellar catalysts have appeared.[7] Mechanistic exploration of these systems is crucial to the construction of useful micellar enzyme analogues.

Recently, we described the comparative effectiveness of micellized surfactants I–IV at catalyzing the cleavages of *p*-



| | I | II | III | IV |
|---|---|---|---|---|
| $R_1$ | $CH_3$ | $CH_3$ | $CH_3$ | $CH_2CH_2OH$ |
| $R_2$ | $CH_3$ | $CH_2CH_2OH$ | $CH_2Im$[12] | $CH_2Im$[12] |

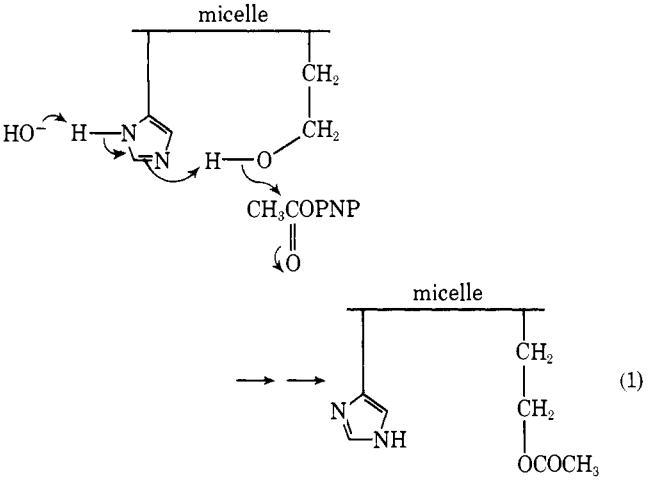
nitrophenyl acetate and hexanoate (PNPA and PNPH).[10] Based upon relative $k_\psi^{max}$ values,[11] there seemed to be no synergism between the hydroxyl and imidazole moieties of IV and no reason to suspect significant differences in mechanistic behavior between III and IV. However, although the reaction of III with PNPA leads to the formation and decay of an acetylimidazole intermediate,[6g] readily observable at 245 nm (Figure 1, curve 1), we can observe no such intermediate during the analogous reaction of bifunctional catalyst IV (Figure 1, curve 2).[13]

From a preparative scale reaction of PNPA with IV,[14] we quantitatively isolated *O*-acetyl-IV.[15] Thus PNPA did not acetylate water under the influence of the bifunctional catalyst. The failure of IV to furnish an observable acetylimidazole intermediate in its reaction with PNPA can be explained in two ways: (a) No intermediate is visible because none is ever formed; IV behaves as a chymotrypsin analogue and undergoes direct *O*-acetylation, eq 1. (b) Alternatively, an intermediate

**Table I.** Pseudo-First-order Rate Constants for Acylation and Deacylation of Micellar Catalysts[13]

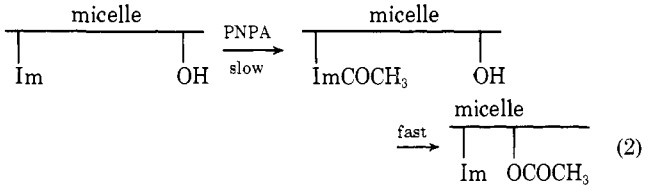
| Case | Catalyst | Substrate | $k_{acyl}$ ($s^{-1}$)[a] | $k_{deacyl}$ ($s^{-1}$)[b] | Rel $k_{deacyl}$ |
|---|---|---|---|---|---|
| 1 | III | PNPA | 0.051 ± 0.003 | 0.015 ± 0.002 | 1.0 |
| 2 | III | PNPH | 0.16 ± 0.01 | 0.020 ± 0.002 | 1.3 |
| 3 | IV | PNPA | 0.038 ± 0.002 | 0.6[c] | ≥40 |
| 4 | IV | PNPH | 0.140 ± 0.005 | 0.18 ± 0.04 | 12 |
| 5 | IV-OAc | PNPA | 0.027[d] | 0.013[d] | 0.87 |
| 6 | IV + I[e] | PNPA | 0.016 ± 0.001 | 0.06 ± 0.01 | 4.0 |
| 7 | IV + I[e] | PNPH | 0.032 ± 0.002 | 0.04 ± 0.01 | 2.7 |
| 8 | III + II[f] | PNPA | 0.036 ± 0.002 | 0.17 ± 0.03 | 11 |
| 9 | III + II[f] | PNPH | 0.081 ± 0.004 | 0.10 ± 0.02 | 6.7 |

[a] From the release of *p*-nitrophenolate ion, monitored at 400 or 440 nm. All quoted errors are average deviations from mean values. [b] Monitored at 245.5 nm (PNPA) or 246.5 nm (PNPH). Acylation and deacylation were treated as consecutive first-order reactions.[16] [c] This is a lower limit estimated assuming 0.02 absorbance units as the detection threshold of *N*-acetyl-IV and $\epsilon_{245.5}^{N\text{-Ac-IV}} = 2160$ (value of $\epsilon^{N\text{-Ac-III}}$). Consecutive first-order reaction analysis ($\beta_{max}$ method) was applied.[16] [d] Single run. [e] [I] = $2.5 \times 10^{-2}$ M; [IV] = $5.0 \times 10^{-3}$ M. [f] $5.0 \times 10^{-3}$ M in *each* surfactant.




(1)

is not observed because it does not build up to a detectable concentration; in a two-step mechanism, eq 2, "slow" N-acetylation of IV is followed by rapid, hydroxyl-mediated deacetylation. A priori, and in either case, the key imidazole




(2)

and hydroxyl moieties could be on the *same* surfactant molecule (intramolecular) or on *adjacent* surfactant molecules within a single micelle (intermolecular).

We now summarize experiments which implicate the sequential (eq 2) rather than the cooperative mechanism (eq 1) in the reaction of IV with PNPA; demonstrate that the sequential process is largely intermolecular; and set a lower limit to the rate constant for the very rapid hydroxyl-mediated deacetylation of N-acetylated-IV.

(1) Reaction of micellar IV with PNPH[13] leads to clearly observable formation and decay of *N*-hexanoyl-IV. From the time dependence of its 246.5-nm absorption, $k_{deacyl}$ was extracted[16] (Table I, case 4). Although deacylation of *N*-hexanoyl-IV is rapid ($k^{IV}_{deacyl}/k^{III}_{deacyl} = 9.0$, cases 4 and 2), *N*-hexanoylation of IV is also rapid ($k^{IV}_{deacyl}/k^{IV}_{acyl} = 1.3$, case 4), and the intermediate can be observed. The reaction of PNPH and IV therefore follows mechanism 2, strongly suggesting that the analogous substrate, PNPA, follows the same mechanism. With PNPA, an unfavorable ratio of the rates of acylation (slow) and deacylation (fast) must prevent accumulation of *N*-acetyl-IV. Based on its nonobservation with

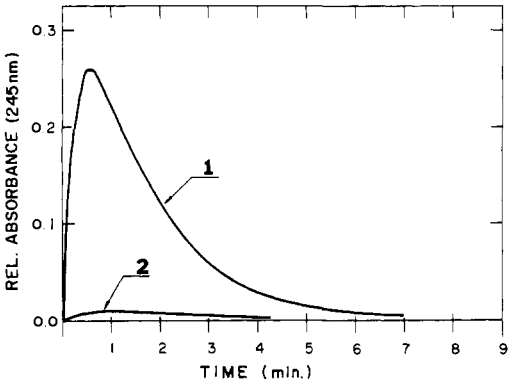



**Figure 1.** Relative absorbances at 245 nm during cleavage of PNPA by micellar III (curve 1) and IV (curve 2).[13]

PNPA, where $k_{acyl} = 0.038$ $s^{-1}$ (case 3), we estimate[16] that $k_{deacyl}$ for *N*-acetyl-IV must be at least 0.6 $s^{-1}$ under our conditions.[13] This is reasonable because $k_{deacyl}$ for *N*-hexanoyl-IV is 0.18 $s^{-1}$, and deacetylation of *N*-acetyl-IV should be more rapid than dehexanoylation (in a hydroxyl-mediated process; see below, and cases 8 and 9).

(2) Reaction of PNPA and IV, comicellized with fivefold excess I, affords *N*-acetyl-IV, now observable at 245.5 nm. We interpret this experiment as follows. In undiluted micellar IV, deacetylation of *N*-acetyl-IV involves both intermolecular and intramolecular acetyl transfers to hydroxyl groups. Comicellization of IV with excess I affords micelles in which each molecule of IV is largely surrounded by molecules of I. Intermolecular deacetylation of *N*-acetyl-IV is inhibited, and the overall rate of deacetylation is reduced. Inspection of Table I (cases 6 and 3) shows that 5:1 dilution of IV with I yields at least a tenfold decrease in the observed $k^{IV}_{deacyl}$. More importantly, from the viewpoint of spectroscopic detection, $k^{IV}_{deacyl}/k^{IV}_{acyl}$ is reduced from 15.8 (minimum value) to 3.75.[17,18]

Under our conditions, the major deacylation pathway for *N*-acyl-IV appears to be *intermolecular*:[19] fivefold dilution of IV with I (which may not suffice to quench all intermolecular deacylation) destroys more than half of the enhancement of $k_{deacyl}$ (relative to $k^{III}_{deacyl}$) initially brought about by functionalization of III with the hydroxyethyl substituent. (Compare $k_{deacyl}$ for cases 3, 6, and 1, and for cases, 4, 7, and 2.)

(3) Intermolecular hydroxyl-mediated deacylation of *N*-acylimidazole surfactants can be independently demonstrated. Deacylations of *N*-acyl-III in 1:1 comicelles of III and hydroxyethyl surfactant II are 11 (deacetylation) and 5.0 (dehexanoylation) times faster than deacylation in micellar III

alone (cases 8 vs. 1 and 9 vs. 2). *O*-Acetyl-II was isolated from the III + II + PNPA experiment. Further, the enhancement of $k_{deacyl}$, relative to $k^{III}_{deacyl}$, is greater with micellar IV than with the 1:1 III + II comicelle (cf. cases 3, 8, and 1, and 4, 9, and 2). The additional enhancement can probably be ascribed to intramolecular N-to-O acyl transfer. Finally, the reaction of PNPA with micellar *O*-acetyl-IV[15] affords a spectroscopically observable *N,O*-diacetyl derivative. Because free hydroxyl groups are unavailable for either intermolecular or intramolecular N-deacylation of this intermediate, $k_{deacyl}$ is small and similar to that of *N*-acetyl-III (cases 5 vs. 1).

The weight of assembled evidence thus leads us to prefer mechanism 2 for the cleavage of *p*-nitrophenyl esters by micellar IV; independent studies by Tonellato afford the same conclusion.[20] Although cooperative catalysis was not observed with IV, we did uncover an extremely facile, sequential process, in which a micellar imidazole-functionalized surfactant cleaves an ester, then rapidly acylates a proximate hydroxyl group. The catalytic advantage of the first step ($k_\psi^{max}/k_o^{buffer}$) is 930.[10] Because this is the rate determining step of the sequence, it confers an effective catalytic advantage of ~37 on the acylation of the hydroxyl function, relative to the acylation of pure micellar II by PNPA.[10] We are continuing our studies of multifunctional micellar catalysts.[21]

**Acknowledgments.** We are grateful to the National Science Foundation and to the Public Health Service (Research Grant CA-14912 from the National Cancer Institute) for financial support. R.A.M. thanks the Dyson Perrins Laboratory, University of Oxford for its hospitality.

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(11) $k_\psi^{max}$ is the maximal pseudo-first-order rate constant for *p*-nitrophenolate release (determined at [surfactant] at which substrate is completely bound).

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(13) Conditions: [surfactant] = $5.0 \times 10^{-3}$ M; [substrate] = $2.0 \times 10^{-4}$ M; pH 8.0, 0.4 M phosphate buffer, 25 °C. Unless otherwise specified, these conditions apply to all kinetic experiments. Cmc's were III, $7.9 \times 10^{-5}$ M and IV, $6.8 \times 10^{-5}$ M, in 0.01 M phosphate buffer.[10]

(14) Conditions: [PNPA] = $1.0 \times 10^{-3}$ M and [IV] = $5.0 \times 10^{-3}$ M in 50 ml of 1.1 M aqueous KCl; titrant, $1.11 \times 10^{-1}$ M aqueous NaOH, pH-stat-titrimeter at pH 8.0. After the consumption of 1 equiv of base, acidification (HCl to pH 1.5) and lyophilization of the product, followed by ethereal washing, extraction with 3:1 acetone–methanol, and precipitation with ether, afforded a mixture of IV·HCl and *O*-acetyl-IV·HCl,[15] the IR spectrum of which was superimposable on that of an authentic 84:16 (the anticipated molar ratio) mixture; cf. especially, the ester carbonyl band at 1740 $cm^{-1}$.

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(17) The apparent $k_{acyl}$ is also depressed upon dilution of IV with I (factor of 2.4) because PNPA is bound to "inert" regions of the comicelle. But $k_{deacyl}$ is more sharply diminished, leading to an observable accumulation of *N*-acetyl-IV.

(18) Parallel experiments with PNPH indicate a 4.5-fold decrease of $k_{deacyl}$ upon fivefold dilution with I, cases 7 vs. 4. Here, however, there is a proportionate decrease in $k_{acyl}$.

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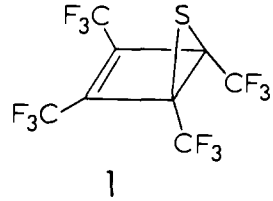
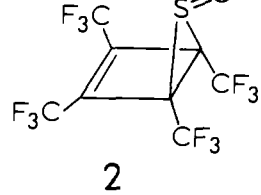
## Automerization of a Dewar Thiophene and Its *exo*-*S*-Oxide. A Dramatic Contrast

*Sir:*

As the only known Dewar isomer of a thiophene, perfluorotetramethyl(Dewar thiophene) (**1**)[1] is an especially interesting compound both from structural and dynamical points of view. This report concerns $^{19}F$ DNMR studies of **1** and its *exo*-*S*-oxide (**2**) which reveal a marked difference between the rates of intramolecular exchange in **1** and **2**.




1




2

Examination of the $^{19}F$ DNMR spectrum (56.4 MHz) of **1** (1.0 M in 1,2,4-trichlorobenzene) at 94 °C (Figure 1) shows two quartet resonances at 13.10 and 15.99 ppm ($^5J_{FF}$ = 2 Hz) downfield from external trifluoroacetamide, consistent with the structure of **1**. When the temperature is raised (Figure 1), the $^{19}F$ DNMR spectrum undergoes broadening and coalescence near 190 °C (Figure 1) characteristic of an increasing rate of exchange of trifluoromethyl groups between different