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A SURFACTANT HYDROPEROXIDE

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Summary. The micellar hydroperoxy surfactant n-$C_{16}H_{33}\overset{+}{N}(CH_3)_2CH_2CH_2OOH, CF_3SO_3^-$ cleaves p-nitrophenyl acetate ~500 times faster than the corresponding hydroxy surfactant, and ~20,000 times faster than lyate ion at pH 8.

Choline surfactants, such as 16-OH, have long been of interest as micellar catalysts for the cleavage of aryl carboxylates[1] and phosphates.[2] Cleavage of the former involves rapid attack of conjugate base $16\text{-}O^-$ on the substrate, followed by slower hydrolysis of the resultant, acylated surfactant.[3] Unfortunately, 16-OH is not very acidic (pK_a~12.4[2]), remains largely un-

$\underset{16\text{-}OH}{n\text{-}C_{16}H_{33}\overset{+}{N}(CH_3)_2CH_2CH_2OH,\ X^-}$ $\underset{16\text{-}OOH}{n\text{-}C_{16}H_{33}\overset{+}{N}(CH_3)_2CH_2CH_2OOH,\ CF_3SO_3^-}$

converted to its reactive alkoxide form at moderate pH, and affords only modest esterolysis rate enhancements relative to nonfunctional micellar catalysts, (e.g.) cetyltrimethylammonium chloride (CTACl). For example, micellar 16-OH cleaves p-nitrophenyl acetate (PNPA) only ~12 times faster than CTACl in 0.01 M phosphate buffer at pH 8, 25°.[4]

Accordingly, we considered the preparation of hydroperoxy surfactant, 16-OOH. Hydroperoxy compounds are 3-4 pK units more acidic than their hydroxylic analogues, and peroxide anions are very effective nucleophiles toward PNPA,[5] so that we anticipated enhanced micellar esterolytic reactivity for 16-OOH. Indeed, α-cumene hydroperoxide, solubilized in micellar CTACl cleaves p-nitrophenyl phenylacetate with a limiting kinetic enhancement of 9000, relative to 0.05 M borate buffer, pH 9.45. 30°.[6] In this letter, we report the preparation and kinetic properties toward PNPA of hydroperoxy surfactant 16-OOH.

n-Alkylhydroperoxides are preparable by the action of basic H_2O_2 on n-alkyl mesylates,[7] but analogous treatment of the triflate derivative of 16-OH (16-OTf)[8] led to mixtures of 16-OOH and 16-OH, rich in the latter. Better results were obtained upon treatment of 16-OTf with 90% H_2O_2 containing 1% sulfuric acid.[9a,b] The final product was a mixture of 16-OOH and 16-OH (as triflate salts), with 16-OOH typically constituting 60-70% of the total; one preparation contained 80% of the hydroperoxide by iodometric determination.[12] Nmr revealed the CH_2OOH absorption at $\delta^{TMS}_{CDCl_3}$ 4.50, deshielded 0.44 ppm from the CH_2OH absorption of 16-OH, OTf^-.[13] A comparable $\alpha\text{-}CH_2$ differential shift was observed for n-butanol/n-butyl hydroperoxide.[7b] Reduction of 16-OOH/16-OH, OTf^- with aq. $NaBH_4$ returned 16-OH, OTf^- (nmr).

Triflate surfactants are not very water soluble, but 16-OOH, OTf^- could not be subjected to anion exchange[8] without extensive decomposition. Kinetic studies therefore employed aqueous co-micellar 16-OOH/16-OH, OTf^- and CTACl (molar ratio 2:1). Figure 1 shows the pseudo-first-order (k_ψ) rate constant vs. [total surfactant] profile for the cleavage of 2×10^{-5} M PNPA by 60% 16-OOH/

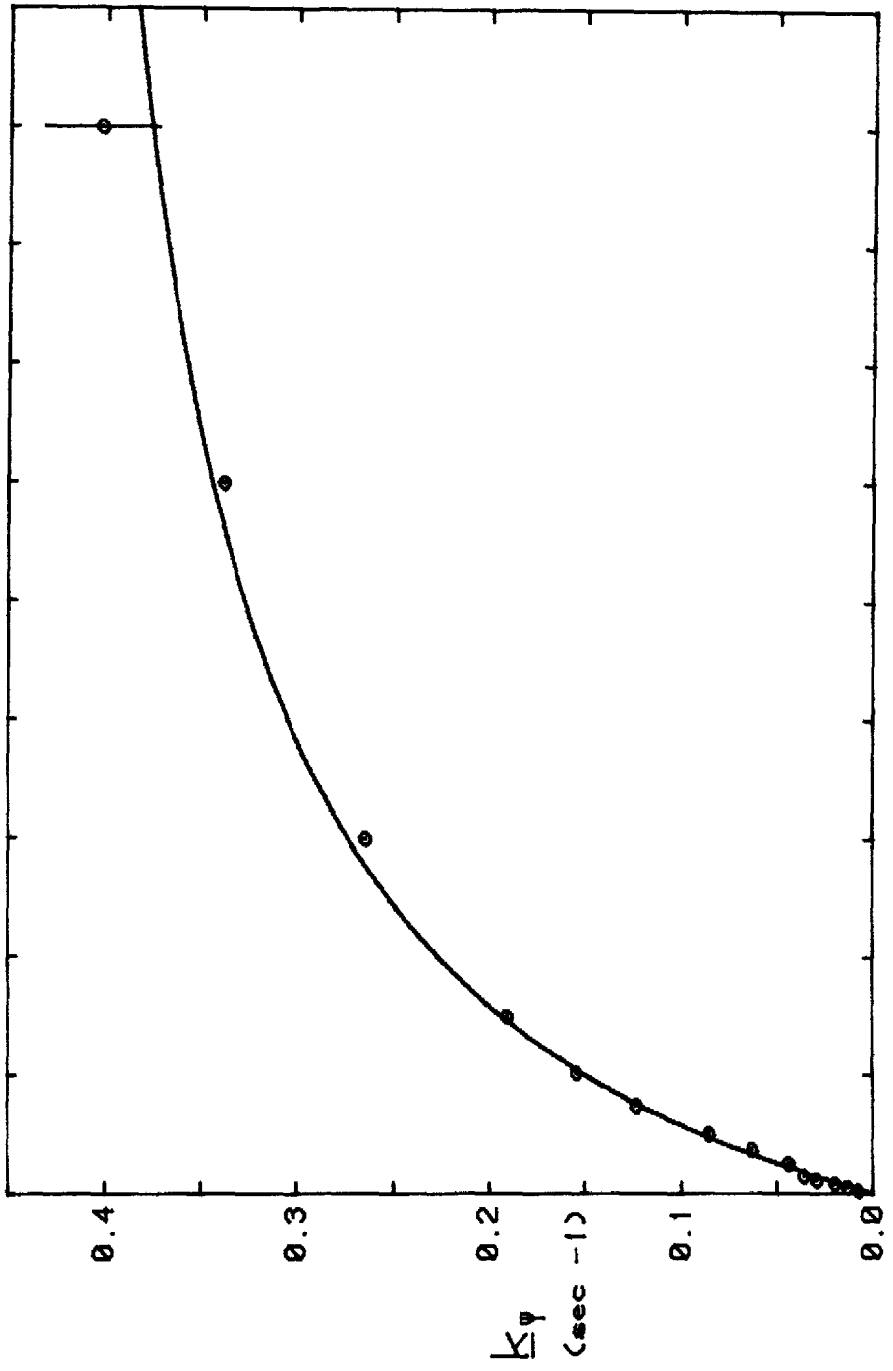

Figure 1. k_ψ vs. [total surfactant] for the cleavage of PNPA by 16-OOH at pH 8; see text for other conditions. Error bars (±7%) are shown for k_ψ^{max}, but average deviations were generally <<5% for other entries, and error bars are omitted.

40% 16-OH (2:1 with CTACl) in 0.02 M phosphate buffer, pH 8, μ = 0.05 (KCl), 25°.[14]

At [total surfactant] = 0.045 M, k_ψ = 0.40 ± 0.03 sec^{-1}, corresponding to a micellar advantage (k_ψ/k_o) of 20,000 vs. buffer alone (k_o = 1.98×10^{-5} sec^{-1}). An analogous profile (not shown) was determined for 16-OH, OTf^-[15] comicellized with CTACl (2:1). k_ψ^{max} = 0.00175 sec^{-1} was observed at [total surfactant] = 0.015 M, indicating a considerable catalytic advantage for 16-OOH. A more quantitative comparison can be made at [total surfactant] = 7.5×10^{-3} M, where purer 16-OOH preparations were studied. Here, 16-OOH/16-OH reagents containing 60, 73, and 80% 16-OOH, afforded k_ψ values of 0.191, 0.334, and 0.573 sec^{-1}, respectively. The latter value is comparable to 0.00121 sec^{-1} for 16-OH, OTf^-, affording a kinetic advantage of 473 for the hydroperoxy surfactant over its hydroxylic analogue. Considering that the several 16-OOH/16-OH reagents, after comicellization with CTACl, are only 40-53% hydroperoxy-functionalized, the apparent kinetic advantage is a minimum.

More detailed analysis of the reactivity of 16-OOH is difficult because we lack data for 16-OOH holomicelles. Nevertheless, some estimates are possible. A pH-rate profile (pH 6.4-10.8) for the cleavage of PNPA by comicellar 60% 16-OOH (5×10^{-4} M) and CTACl (2.5×10^{-4} M) gave $pK_a^{16\text{-OOH}}$ ~9.6. Superficially, it appears that the pH 8 kinetic advantage of micellar 16-OOH over micellar 16-OH (~500) is mainly attributable to their differential acidity ($\Delta pK \sim 2.8$), leaving little room for extra enhancement due to the operation of an α-effect with 16-OOH. In this, $16\text{-}OO^-$ and $16\text{-}O^-$ resemble CH_3OO^- and CH_3O^-, where little difference is observed in the rate constants for PNPA cleavage.[5] However, it would be wrong to exclude an α-effect contribution to the intrinsic reactivity of 16-OOH. Approximate log k_2 (1/mol-min) values for the cleavage of PNPA by $16\text{-}OO^-$ and $16\text{-}O^-$ (both ~5.5) may be compared to values anticipated from Brønsted correlations of log k_2 vs. pK_a for alkoxides/phenoxides[16] or peroxides.[17] We find $16\text{-}O^-$ to be ~100 times more reactive toward PNPA than an alkoxide of comparable pK, which can be attributed to micellar catalysis. Micellar $16\text{-}OO^-$ is ~6000 times more reactive than an alkoxide of comparable pK, and ~15 times more reactive than a comparable peroxide. Both micellization and an α-effect would therefore appear to contribute to the enhanced esterolytic reactivity of 16-OOH, relative to comparably acidic ROH.

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(9) (a)A.G. Davies and R. Field, J. Chem. Soc., 4637 (1958). (b) Twenty ml of 0.25 M 16-OTf, OTf^- in CH_2Cl_2[8] was added dropwise to 15 ml of stirred 90% H_2O_2, containing 1% H_2SO_4, at 0^o. Stirring was continued at 25^o for 24 hrs, followed by hydrolysis (90 ml H_2O), and lyophilization to a yellow-white solid, which was dissolved in 25 ml of abs. ethanol. Solvent evaporation afforded a white solid which was dissolved in 25 ml of CH_2Cl_2 and extracted with 100 ml of H_2O to remove retained H_2O_2.[10] Stripping of the CH_2Cl_2 returned the solid product. Two-fold repetition of the CH_2Cl_2/H_2O procedure afforded a product of constant iodometric[12] peroxide content.

(10) Lipophilic quaternary ammonium ions extract H_2O_2 into nonpolar media,[11] so that back-extraction is essential. In a control experiment, 16-OH, OTf^- (see below) was subjected to the entire procedure of ref. 9b; recovered 16-OH, OTf^- contained <1% peroxide.[12]

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(13) 16-OH, OTf^-, mp 120-121^o was prepared by triflic acid precipitation of aq. 16-OH, Br^-. A satisfactory elemental analysis (C,H,F) was obtained.

(14) Reactions were followed by stopped-flow or conventional spectroscopy, monitoring the release of p-nitrophenoxide ion at 400 nm.

(15) This material was first subjected to the H_2O_2 reaction and workup conditions described in ref. 9b.

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