

PREDICTED RATE ENHANCEMENTS OF DEPHOSPHORYLATION IN FUNCTIONAL OXIMATE COMICELLES

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Abstract. The rate enhancements of dephosphorylation of p-nitrophenyldiphenyl phosphate by comicelles of cetyltrimethylammonium bromide with a functional cosurfactant are due wholly to increased concentration of the nucleophile in the micelle.

Functional micelles and comicelles are effective nucleophilic reagents.¹ Typical reactive groups are imidazole, oxime, hydroxamic acid, hydroxyl or thiol which may be deprotonated at high pH to give nucleophilic anionic moieties. Rate enhancements, over those for reaction with nonmicellized nucleophile, could be caused by: (i) a high nucleophile concentration in the Stern layer at the micelle-water interface, (ii) increased deprotonation at this interface, and (iii) some special rate enhancement by the micelle.

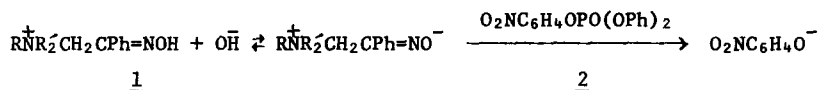
A simple model suggests that only effects (i) and (ii) are important and that the rate constant for micellar bound substrate can be predicted from the second order rate constant for reaction of a similar but monomeric nucleophile in water.²⁻⁵

Second order rate constants, k_2^m , estimated in terms of the volume of the micelle, or its Stern layer, are similar to or slightly less than those in water, k_w , i.e., the rate enhancement is due almost wholly to concentration of reactants in the micellar pseudophase.²⁻⁵ By estimating the volume of the Stern layer of micelles of cetyltrimethylammonium bromide (CTABr) we estimate that the molar concentration of a nucleophilic reactant in the micelle is ca. $7n$, where n is its mole fraction in the micelle.^{3,6} If $k_2^m \approx k_w$, in functional as in nonfunctional micelles,²⁻⁵ application of this model to reaction in a functional comicelle leads to the following relation between k_w and the first order rate constant, k_ψ^{max} , for a fully micellar bound substrate:³

$$k_\psi^{max} \approx 7nk_w$$

This model fits rate enhancements in micelles of a hydroxyethyl surfactant,³ provided that correction is made for incomplete deprotonation of the hydroxyl group, and our aim was to test it using a fully deprotonated nucleophilic head group and a fully micellar bound substrate.

We used the oxime, 1a,⁷ which because of its low solubility was comicellized with CTABr. The substrate was p-nitrophenyldiphenyl phosphate, 2.



1a, R = C₁₂H₂₅, R' = Me; 1b, R, R' = Et

Reaction with a suitable model, 1b, gives $k_w = 0.92 \text{ M}^{-1}\text{s}^{-1}$ at 25.0°C (pH 10 and 11, carbonate buffer). Results for reaction in comicelles of 1a and CTABr are in Table 1. (Allowance has been made for the small contribution of reaction with OH^-).⁸ The binding constant of 2 to CTABr is ca. $2 \times 10^4 \text{ M}^{-1}$, so 2 should be fully micellar bound under most conditions in Table 1.⁴

Table 1 Dephosphorylation in Comicelles of 1a and CTABr^a

$10^4 [1], \text{ M}$	$[1a]/[\text{CTABr}]$		
	1/5	1/10	1/15
1	0.36(2.3)	0.26(3.1)	0.13(2.3)
5	0.33(2.2)	0.25(3.0)	0.13(2.3)
15	0.36(2.3)	0.30(3.6)	0.18(3.1)
25	0.37(2.4)	0.30(3.6)	0.18(3.1)

a) Values of $k_\psi, \text{ s}^{-1}$ at 25.0°C in 0.01 M OH^- , corrected for reaction of OH^- .
Values in parentheses are k_ψ^{max}/nk_w for fully bound 2.

If we neglect the small concentration of monomeric surfactant the simple model predicts a value of $k_\psi^{\text{max}}/nk_w \approx 7$, whereas the actual values vary between 2 and 3 (Table 1). These slightly lower than predicted values are understandable, because in nonfunctional micelles k_w is generally slightly larger than $k_2^{\text{m} 2-5}$, and the Stern layer volume of a functional comicelle may be larger than that of CTABr.

Our results suggest that the major source of the rate enhancements is the same in functional and nonfunctional micelles, viz, increased reactant concentration in the micellar pseudophase.²⁻⁵ However unless $\text{pH} > \text{pK}_A$ for deprotonation of the functional group deprotonation will also be important.³ Thus effects (i) and (ii) must be considered; but (iii) plays at most a minor role in catalysis by functional micelles or comicelles.

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