

one exception: hydrogenation of acetylene to ethylene proceeded in conversions comparable to that on Pd(111).

Palladium's unique catalytic activity under ultrahigh vacuum conditions has been demonstrated for three different classes of catalytic reactions: cyclizations of alkynes, alkyne addition reactions, and hydrogenation reactions of a variety of unsaturated molecules. Probably, there are several contributing factors, and rather than speculating on the basis for palladium's apparently unique position in the triad, we plan to extend these studies (i) to rhodium and silver, (ii) to other classes of catalytic reactions, and (iii) to metal films at low to medium pressures. We also plan to use NEXAFS (near-edge X-ray absorption fine structure spectra) to establish molecular orientations over the course of these catalytic reactions.

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Supplementary Material Available: Experimental procedure and conditions (1 page and Table I) and Figures 1-5 depicting the thermal desorption spectra for Pd(111)-propyne, Pd(111)-D-C₂H₂, Pd(111)-D-C₂H₂(corrected), Pd(111)-C₂H₂-(CH₃)₃-SiH, and Pd(111)-D-CD₃CN (9 pages). Ordering information is given on any current masthead page.

Dynamic Behavior of a Two-Site Vesicular Reaction

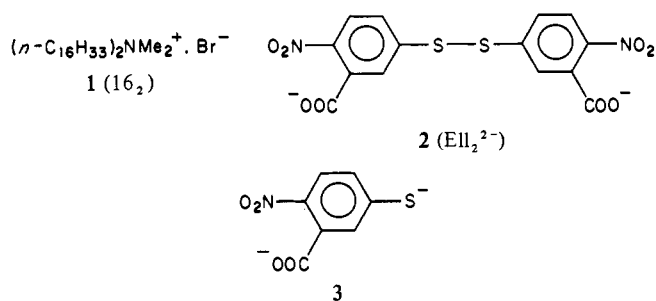
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Surfactant vesicles possess exterior and interior membrane surfaces and interior volumes.¹ When a chemical reaction takes place in a vesicular environment, it is sometimes possible to kinetically resolve the portion occurring on the vesicular surface (exovesicular) from the portion that occurs at interior sites (endovesicular).²⁻⁴ Here, we report the first example of a two-site vesicular reaction in which each reaction can be kinetically differentiated and the time course of substrate distribution between the two sites can be quantitatively followed.

The reaction is the pH 8 cleavage in vesicular **1** of Ellman's reagent (**2**) by excess dithionite ion, affording the chromophoric



(1) Fendler, J. H. *Acc. Chem. Res.* **1980**, *13*, 7. Kunitake, T.; Shinkai, S. *Adv. Phys. Org. Chem.* **1980**, *17*, 435. Fendler, J. H. "Membrane Mimetic Chemistry"; Wiley: New York, 1982.

(2) Moss, R. A.; Bizzigotti, G. O.; Ihara, Y. In "Biomimetic Chemistry"; Yoshida, Z.-I., Ise, N., Eds., Kodansha: Tokyo, 1983; pp 189-205.

(3) Moss, R. A.; Ihara, Y.; Bizzigotti, G. O. *J. Am. Chem. Soc.* **1982**, *104*, 7476.

(4) Moss, R. A.; Bizzigotti, G. O. *J. Am. Chem. Soc.* **1981**, *103*, 6512.

Table I. Cleavage of Ellman's Reagent by Dithionite Ion^a

case	surfactant	conditions	method ^b	$k_{\psi}^f, \text{s}^{-1}$ ^c	$k_{\psi}^s, \text{s}^{-1}$ ^d
1	none	aq soln	A	$0.177 \pm 0.004_4$	none ^e
2	CTAB ^f	micelle	B	$61 \pm 3_3$	none ^e
3	16_2	vesicle ^g	C	$176 \pm 3_3$	none ^e
4	16_2	vesicle ^g	B	$175 \pm 9_5$	$2.0 \pm 0.1_{2,2}$
5	16_2	vesicle ^{g,h}	B	$160 \pm 20_3$	$2.1 \pm 0.2_{2,2}$
6	16_2	vesicle ^{g,i}	B	$150 \pm 8_5$	$1.5 \pm 0.2_{1,1}$

^a Conditions (after reagent mixing): [surfactant] = 5.0×10^{-4} M, [2] = 2.5×10^{-5} M, [$\text{S}_2\text{O}_4^{2-}$] = 5.0×10^{-4} M, pH 8.0, 0.01 M Tris buffer, $\mu = 0.01$ (KCl), 25 ± 0.2 °C. Anion **3** was monitored at 400 or 450 nm in aqueous or surfactant solutions, respectively.

^b Method A: stopped-flow experiment in which buffered solutions of **2** and $\text{S}_2\text{O}_4^{2-}$ were mixed. Method B: multimix configuration in which solutions of surfactant and **2** were mixed (<1 ms) followed, after a delay of 46 ms, by mixing (<1 ms) with $\text{S}_2\text{O}_4^{2-}$ solution. Method C: multimix configuration but with an inverse mixing order: (surfactant + $\text{S}_2\text{O}_4^{2-}$) followed by **2**. ^c Observed rate constant of "fast" reaction; errors are standard deviations of n (subscript) runs. ^d Observed rate constant of "slow" reaction; errors as in *c*. For percentages of slow reactions see Table II under 46-ms age time. ^e Only monophasic kinetics were observed. ^f Cetyltrimethylammonium bromide. ^g Vesicles were generally prepared by sonication of **1** at 60-65 °C using a Braun-Sonic Model 1510 probe type sonifier operated at 70 W for 30-45 min. Vesicle solutions were filtered through 0.8- μm Millipore "Millex-PF" filters before use. ^h Twenty weight percent cholesterol was cosonicated with 16_2 during vesicle preparation. ⁱ One equivalent (1×10^{-4} M) of 18-crown-6 was added to the solution of **2**.

anion **3**.⁵ Table I records rate constants obtained by rapid mixing kinetic techniques under a variety of conditions. Most experiments employ a Durrum model D-132 multimixing unit in which solutions A and B mix (<1 ms) and, after an adjustable aging period (≥ 46 ms in our system), (A + B) rapidly mixes with C (<1 ms) and enters a stopped-flow cuvet for spectral analysis.⁶

Comparison of cases 2 and 1 (Table I) shows that the pseudo-first-order cleavage of **2** to **3** by excess $\text{S}_2\text{O}_4^{2-}$ is ~ 340 times faster in micellar CTAB than in water. Catalysis is anticipated for the reaction of two anions in a cationic micelle.⁷ In case 3, empty vesicles of **1**⁸ are first mixed with $\text{S}_2\text{O}_4^{2-}$ and then with Ell_2^{2-} ("inverse addition"). Cleavage of Ell_2^{2-} is ~ 1000 times faster than in water. This vesicular reaction is kinetically monophasic, and we assign its locus as the vesicular surface (exovesicular).^{7b,9}

When, however, Ell_2^{2-} was added before $\text{S}_2\text{O}_4^{2-}$ (case 4), two sequential reactions were observed. The faster process, $k_{\psi}^f \sim 175 \text{ s}^{-1}$ (80%), was again the exovesicular reaction, but it was followed by a considerably slower reaction, $k_{\psi}^s \sim 2 \text{ s}^{-1}$ (20%). Cases 5 and 6 show that similar pairs of sequential reactions are observed when the 16_2 vesicles are doped with 20% cholesterol or when an equivalent of 18-crown-6 is added to the Ell_2^{2-} solution.¹⁰

We suggest that addition of Ell_2^{2-} to empty 16_2 vesicles initially gives exovesicularly-sited Ell_2^{2-} , which slowly permeates the vesicular surface and occupies a second, subsurface site. Addition

(5) The cleavage of **2** to **3** by OH^- has been studied in micellar and vesicular systems: Fendler, J. H.; Hinze, W. L. *J. Am. Chem. Soc.* **1981**, *103*, 5439. The pK_a 's of **2** (4.75) and **3** (4.53) indicate complete ionization at pH 8.

(6) Absorbance data were acquired by a photomultiplier tube linked to a custom-built interface and transferred for analysis to a Commodore CBM 8032 computer equipped with a dual floppy-disc drive and high-resolution graphics.

(7) (a) Bunton, C. A. *Catal. Rev.-Sci. Eng.* **1979**, *20*, 1. (b) Fendler and Hinze⁵ report 15- and 1500-fold accelerations (vs. H_2O) for OH^- cleavage of **2** in micellar CTAB and vesicular dioctadecyldimethylammonium chloride, respectively. The vesicular binding constant of **2** is given as $\sim 1.4 \times 10^4 \text{ M}^{-1}$.

(8) Vesicles prepared according to the method of note g, Table I, had $d \sim 520 \text{ \AA}$ by dynamic light scattering ($d \sim 600 \text{ \AA}$ when 20 wt % of cholesterol was cosonicated with 16_2). Our experience with electron microscopic analysis of vesicular **16**, suggests that these vesicles probably contain several lamellae.

(9) Cationic and anionic surfactant vesicles are impermeable to dithionite ions: Baumgartner, E.; Fuhrhop, J.-H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 550. Lee, L. Y.-C.; Hurst, J. K.; Politi, M.; Kurihara, K.; Fendler, J. H. *J. Am. Chem. Soc.* **1983**, *105*, 370.

(10) The $[\text{K}^+]$ due to background electrolyte is $3.5 \times 10^{-3} \text{ M}$.

Table II. Effect of Aging on the Biphasic Vesicular Cleavage of Ellman's Reagent^a

age, s ^c	percent slow reaction ^b		
	vesicular 16 ₂ ^d	20% cholesterol/16 ₂ ^e	18-crown-6/16 ₂ ^f
0.046	20.1	25.5	47.6
0.071	<i>g</i>	<i>g</i>	53.8
0.096	25.5	41.2	61.0
0.146	36.8	54.5	66.1
0.246	45.4	60.0	72.1
0.346	49.7	65.0	81.0
0.446	54.0	66.8	80.9
0.546	58.0	66.9	
0.796	61.1	70.4	
1.05	62.8	71.0	
5.05	64.6	<i>g</i>	
10.0	64.6	71.1	
60.0	<i>g</i>	<i>g</i>	79.0
cosonicate ^h	70.2	66.5	<i>g</i>

^a Conditions as in Table I, note *a*. Method B was used for sequential multimixing of reagents; see Table I, note *b*. ^b The percent of slow reaction was calculated from the absorption change corresponding to the slow process vs. the total absorbance change. The difference between 100% and the tabulated percent slow reaction equals percent fast reaction. ^c Time between mixing of 16₂ vesicles with **2** and addition of S₂O₄²⁻. ^d Empty vesicles; Table I, note *g*. ^e Table I, note *h*. ^f Table I, note *i*. ^g Not determined. ^h Reagent **2** was cosonicated with vesicular 16₂ for 5 min at 60 °C and 70 W. 16₂/2 and dithionite were then mixed in a stopped-flow experiment.

of S₂O₄²⁻ then affords reactions at both sites with different rate constants.¹¹ This scheme is supported by the variable aging experiments recorded in Table II. When the 16₂ + Ell₂²⁻ solutions are aged 46 ms before S₂O₄²⁻ addition, 80% of the overall reaction is exovesicular (fast) and 20% is subsurface or slow. Increasing the aging time permits more Ell₂²⁻ to reach the subsurface site, and the proportion of the slow reaction increases smoothly to a maximum of ~65% in 1–5 s. The final distribution represents substrate equilibration between exovesicular and subsurface sites; note that cosonication of Ell₂²⁻ with 16₂, followed by stopped-flow

(11) The precise mechanism of the S₂O₄²⁻/Ell₂²⁻ reaction is not yet established. In either buffer or vesicular **1**, excess S₂O₄²⁻ generates only 1 equiv of **3** from **2** (as compared to 2 equiv of **3** when dithiothreitol is used). This suggests that aqueous S₂O₄²⁻ may provide nucleophilic HSO₃⁻, which cleaves **2** to **3** and ArSSO₂⁻. Cf.: Castaldi, G.; Perdoncin, G.; Giordano, C. *Tetrahedron Lett.* **1983**, *24*, 2487.

reaction with S₂O₄²⁻, affords a similar slow/fast distribution of reactions (Table II).

Indeed, these data give a reasonable fit to integrated equations describing the approach to equilibrium of the (first-order) system A ⇌ B.¹² Analysis gives *k*₁ ~ 2.1 s⁻¹ and *k*₋₁ ~ 1.2 s⁻¹, where *k*₁ represents the exovesicular to subsurface exchange and *k*₋₁ denotes the reverse process.

Table II reveals that similar phenomena occur with cholesterol-doped 16₂ vesicles and when 18-crown-6 is added to the Ell₂²⁻ solution. In the latter case, the maximum contribution of the slow reaction is significantly greater than in the absence of crown ether and is reached more rapidly. The cholesterol-doped 16₂ vesicles occupy an intermediate position in terms of the maximum contribution of the slow process and the aging time required to achieve it. It should be noted that although aging affects the slow/fast reaction distribution, the rate constants are unaffected.

The catalyzed dithionite cleavages of vesicle-bound Ell₂²⁻ occur at two sites, and equilibration of the substrate between these sites requires ~0.35–5 s, depending on the experimental conditions. One site is clearly the vesicular surface. The second site probably corresponds to very shallow penetration by Ell₂²⁻ because dithionite ions do not readily cross hydrophobic membranes,⁹ and although cholesterol should inhibit endovesicular reactions of S₂O₄²⁻,¹³ the data show that the "second-site" reaction is mildly promoted by cholesterol.¹⁴

Accordingly, we consider the second site to be "subsurface", but not "endovesicular". A possible model pictures exovesicular Ell₂²⁻ as initially bound "broadside" (tangentially) on the vesicular surface. With aging of the ensemble, Ell₂²⁻ molecules reversibly migrate to (radial) intercalation sites, between the surfactant monomers, but within the membranes's outer palisade. This location would be less polar than the exovesicular site but still accessible to the dithionite.

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(12) Frost, A. A.; Pearson, R. G. "Kinetics and Mechanism", 2nd ed.; Wiley: New York, 1961; pp 185–186, eq 71. We find (*k*₁ + *k*₋₁) = 3.26 s⁻¹, and we take *k*₁/*k*₋₁ = 1.82 (i.e., 64.6/35.4, Table II, column 2, 5- and 10-s entries).

(13) Moss, R. A.; Hui, Y. *Tetrahedron Lett.* **1983**, *24*, 3961.

(14) Cosonicated 16₂ and Ell₂²⁻ react completely¹¹ with excluding "hidden" endovesicular Ell₂²⁻. This suggests relatively free permeability of Ell₂²⁻ (but not dithionite⁹) between "subsurface" and endovesicular sites.

Additions and Corrections

Toward Tricyclo[2.2.2]decane. 1. [n.2.2.2]Paddlane Systems, n = 10–14 [*J. Am. Chem. Soc.* **1983**, *105*, 1656]. PHILIP E. EATON* and BERNARD D. LEIPZIG

Page 1656, the third line of the second paragraph should read as follows: ...gave, after oxidation,...

Polar Radicals. 17. On the Mechanism of Iodine Atom Transfer. A 9-I-2 Intermediate [*J. Am. Chem. Soc.* **1982**, *104*, 3917]. DENNIS D. TANNER,* DARWIN W. REED, and B. P. SETILOANE
Page 3918: Equations 3 and 4 should read

$$[\text{PhI}]/[\text{PhCl}]\cdot[\text{CCl}_4]/[\text{ArI}] = (k_1/k_{\text{Cl}})[1/(k_{-1}/k_2 + 1)] \quad (3)$$

$$(k_1/k_{\text{Cl}})_{\text{obsd}} = k_1/k_{\text{Cl}}[1/(k_{-1}/k_2 + 1)] \quad (4)$$

The plot of the corrected equation, to replace Figure 3, does not show a significant substituent effect for log (*k*₁/*k*_{Cl}) as originally reported. The conclusions drawn from this plot must, therefore, be modified. The mechanistic implications of this observation will be the subject of a future communication from this laboratory

Measurement of Nonsynergistic Anion Binding to Transferrin by EPR Difference Spectroscopy [*J. Am. Chem. Soc.* **1982**, *104*, 5775]. DONALD A. FOLAJTAR and N. DENNIS CHASTEEN*

Page 5777: Contrary to our statement that no anion effect is observed when iron(III) nitrilotriacetate 1:2 is used to saturate the protein, subsequent experiments have shown that this is not the case. Anion effects on the EPR spectrum occur when the diferric protein is prepared by using either Fe(II) or Fe(III)-NTA.