types; primary (**10**), secondary (**4**, **7**, **8**), and vinylic (**12**), and that the stereochemistry of the cyano center is determined by the relative ease of access to the cyclized radical.

Even at this early stage it seems clear that the process of radical cyclization–trapping will prove synthetically valuable.

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Registry No. 1, 85710-98-1; **4** (isomer 1), 87453-49-4; **4** (isomer 2), 87453-62-1; **4** (cyanolactone), 87453-59-6; **5**, 3212-60-0; **5** (bromoacetal), 87453-50-7; **6**, 3718-58-9; **6** (bromoacetal), 87453-51-8; **7**, 87453-52-9; **7** (cyanolactone), 87453-60-9; **8**, 87453-53-0; **9**, 87453-54-1; **9** (bromoacetal), 87453-55-2; **10**, 87453-56-3; **10** (cyanolactone), 87453-61-0; **11**, 34683-71-1; **11** (bromoacetal), 87453-57-4; **12**, 87453-58-5; *tert*-butyl isocyanide, 7188-38-7; hexaphenylditin, 1064-10-4; bromoacetaldehyde, 17157-48-1.

Catalytic Chemistry of Palladium Surfaces under Ultrahigh Vacuum Conditions

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Reaction steps that may ensue after the chemisorption of a hydrocarbon on a transition-metal surface are thermodynamically a sensitive function of temperature and pressure. Low temperatures and high H_2 pressures, for example, favor C–H bond formation. The unusual conditions employed for some surface science studies, i.e., ultralow pressure and surface coverages of a monolayer or less, are not optimal for hydrogenation (C–H bond formation), addition, and oligomerization reactions. These involve bimolecular reaction steps, which are not favored by low surface coverages (particularly if mobility of surface species is low). Also, the probability of hydrogenation is low because the thermodynamic activity of chemisorbed hydrogen atoms is low at pressures of 10^{-10}–10^{-11} torr. Hence, the typical ultrahigh vacuum–low temperature reaction course for chemisorbed hydrocarbons is dehydrogenation[1-8] although there are well-established exceptions such as the hydrogenation of acetylene chemisorbed on Pt(111) to form Pt(111)–CCH_3.[9-11]

Recently, we have found[12,13] that palladium surfaces under ultrahigh vacuum conditions exhibit a chemistry demonstrably different from those of nickel and platinum. Specifically, acetylene trimerizes to form benzene on the low Miller index planes of palladium.[13,14] Other reactions compete with the trimerization but benzene formation is the major reaction at least on the Pd(111) surface at near saturation coverages provided that acetylene is initially adsorbed at low temperatures, <−100 °C (with these conditions, the conversion was ~25%, whereas benzene formation was a minor reaction at 25 °C). The presence of sulfur on the surface substantially increased the conversion to benzene. Benzene formation in these reactions is presumably acetylene trimerization, a reaction not commonly observed for metallic catalysts but is common[15] to metal coordination catalysts. Interestingly, toluene could be generated as the major product by heating a mixture of propyne and acetylene chemisorbed on Pd(111): the ratio of toluene to benzene was 3:1 from a Pd(111)–propyne–acetylene state formed by chemisorbing (at −120 °C) propyne first. We have also detected significant benzene formation on heating Pd(111)–propyne (Figure 1, supplementary material) and Pd(111)–trimethylsilylacetylene although these reactions are complex and the benzene yields are 10% or less. Use of ^{13}C-labeled propyne molecules may reveal the genesis of benzene in this complex reaction.

Pyridine was formed from acetylene and hydrogen cyanide on Pd(111) in yields of approximately 10%. The acetylene and the hydrogen cyanide were coadsorbed at −110 °C, and then the crystal was heated. Pyridine desorbed at ~100 °C, the characteristic desorption temperature for Pd(111)–NC_5H_5. Attempts to hydrogenate pyridine on this surface were unsuccessful.

On Pd(111) or Pd(100), we have demonstrated the following hydrogenation reactions: acetylene to ethylene (50%), ethylene to ethane (25%), benzene to cyclohexane (5%), and norbornadiene to norbornane (5–10%) as well as olefin formation from propyne, 2-butyne, and 2-pentyne. The typical experimental protocol comprised (i) adsorption of hydrogen (or deuterium) and then adsorption of the hydrocarbon at −130 °C and (ii) the thermal desorption experiment with a heating rate of ~25 °C s^{-1}. Appearance of the hydrogenated product was at ~0 °C (C_2D_4 from $C_2D_2 + D_2$ on Pd(111)), 25 °C (C_2D_6 from $D_2 + C_2D_4$ on Pd(100)), 25 °C (c-C_6D_{12} on Pd(110)), and 10 °C (norbornane on Pd(111)). These temperatures for the appearance of the alkanes are very similar and in the case of ethane and cyclohexane substantially exceed the characteristic desorption temperatures of these alkanes on Pd(111). Hence the onset of rapid hydrogenation in these UHV systems is about at 0–25 °C for these palladium surfaces. In the $C_2H_2 + D_2$ reaction, the major product was $C_2H_2D_2$ (Figures 2 and 3, supplementary material).

Hydrogenation of acetonitrile to ethylamine was also demonstrated. Cochemisorption of D_2 and CD_3CN at 25 °C (Pd(100)) followed by the thermal desorption experiment gave ~5% conversion of CD_3CN to $C_2D_5ND_2$ which desorbed at ~80 °C (Figure 4, supplementary material).

Hydrosilation reactions with acetylene were effected on Pd(111) with conversions of 10–20%. In these experiments, the adsorption was effected at −110 °C with either $(CH_3)_3SiH$ (Figure 5, supplementary material) or $(CH_3)_2SiHCl$ as the silane reagent. Critical to the high conversions (for UHV conditions) was adsorption of the acetylene before the silane (reverse order of addition with respect to hydrogenation reactions). The vinylsilane products, $(CH_3)_3SiCH{=}CH_2$ and $(CH_3)_2SiCl(CH{=}CH_2)$ desorbed from Pd(111) at ~50 °C. Conversions in these reactions were increased by a factor of ~5 using a Pd(111)–P surface (~0.5 monolayer).

The contrast between palladium and its two congeners in UHV catalytic chemistry is sharp. Hydrogenation of benzene could not be demonstrated on Ni(111) under conditions identical with the above-described palladium chemistry, and hydrogenation of acetylene gave only trace conversions to ethylene. Analogous negative results were observed relative to acetylene conversion to benzene and hydrogenation of acetonitrile to ethylamine. The Pt(111) chemistry was identical with that of Ni(111) with only

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0002-7863/83/1505-6766$01.50/0

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–C_2H_2, Pd(111)–D–C_2H_2(corrected), Pd(111)–C_2H_2–$(CH_3)_3SiH$, and Pd(111)–D–CD_3CN (9 pages). Ordering information is given on any current masthead page.

Dynamic Behavior of a Two-Site Vesicular Reaction

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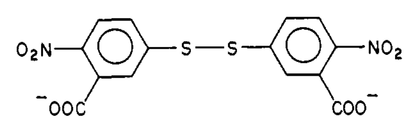
Surfactant vesicles possess exterior and interior membrane surfaces and interior volumes.[1] When a chemical reaction takes place in a vesicular environment, it is sometimes possible to kinetically resolve the portion occurring on the vesicular surface (exovesicular) from the portion that occurs at interior 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 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]

$(n\text{-}C_{16}H_{33})_2NMe_2^+,\ Br^-$

1 (16_2)



2 (Ell_2^{2-})

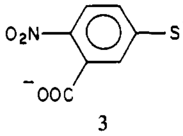


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Table I. Cleavage of Ellman's Reagent by Dithionite Ion[a]

case	surfactant	conditions	method[b]	$k_\psi{}^f$, s^{-1} [c]	$k_\psi{}^s$, 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	$175 \pm 9_5$	$2.0 \pm 0.1_{22}$
5	16_2	vesicle[g,h]	B	$160 \pm 20_3$	$2.1 \pm 0.2_{22}$
6	16_2	vesicle[g,i]	B	$150 \pm 8_5$	$1.5 \pm 0.2_{11}$

[a] Conditions (*after* reagent mixing): [surfactant] = 5.0×10^{-4} M, [**2**] = 2.5×10^{-5} M, [$S_2O_4^{2-}$] = 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 $S_2O_4^{2-}$ 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 $S_2O_4^{2-}$ solution. Method C: multimix configuration but with an inverse mixing order: (surfactant + $S_2O_4^{2-}$) 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**.

Comparison of cases 2 and 1 (Table I) shows that the pseudo-first-order cleavage of **2** to **3** by excess $S_2O_4^{2-}$ 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 $S_2O_4^{2-}$ 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* $S_2O_4^{2-}$ (case 4), two sequential reactions were observed. The faster process, $k_\psi{}^f \sim 175$ s^{-1} (80%), was again the exovesicular reaction, but it was followed by a considerably slower reaction, $k_\psi{}^s \sim 2$ 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

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

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