H), 4.16 (q, 0.55 H), 4.30 (q, 0.45 H), 5.48 (q, 0.55 H), 5.79 (q, 0.45 H); mass spectrum, m/z (relative intensity) 146 (2), 117 (13), 84 (60), 66 (100), 59 (23), 43 (22).

***N*-Nitroso-2,2,5-trimethyl-1,3-oxazolidine (10).** To a solution of 7.5 g (0.1 mol) of 1-amino-2-propanol (8) in 20 mL of water and 20 mL of glacial acetic acid was added 11 mL of acetone. The solution was cooled to 0 °C and 14 g (0.2 mol) of sodium nitrite in 25 mL of water was added dropwise. The solution was stirred at 0 °C overnight, made basic by the addition of potassium hydroxide pellets, and extracted with methylene chloride. The organic layer was washed with 5% hydrochloric acid and 5% sodium bicarbonate and dried over anhydrous sodium sulfate, and the solvent was removed on a rotary evaporator. The residual oil was vacuum distilled to give 1.6 g (11%) of **10**, which was contaminated with **9a** and **9b**: bp 64 °C (0.2 mmHg); IR (film) 2980, 2930, 1455, 1425, 1380, 1300, 1175, 1065, 985 cm^{-1}; NMR ($CDCl_3$) δ 1.4 (d, 3 H), 1.69 (s, 3 H), 1.84 (s, 3 H), 3.11 (m, 1 H), 4.06 (m, 1 H), 4.40 (m, 1 H), signals corresponding to **9a** and **9b** contaminants are not included here. The GLC retention time of compound **10** corresponds to that of the minor component obtained in the deamination reaction of 1-amino-2-propanol (**8**).

Deamination of 2-Amino-1-propanol (12). To a 0.5 M solution of 447 mg (4 mmol) of 2-amino-1-propanol hydrochloride in water was added enough 10% HCl to increase the acidity to pH 4. To the solution was added 3.3 mL of 3.6 M aqueous sodium nitrite. The mixture was stirred at 25° C for 2 h. The solution was extracted with methylene chloride, washed with 5% sodium bicarbonate, and dried over anhydrous sodium sulfate, and the solvent evaporated under vacuum. The residue was vacuum distilled to give an average yield of 96 mg (16%) of (*E*)- and (*Z*)-*N*-nitroso-2-ethyl-4-methyl-1,3-oxazolidines (**13a,b**) in a 2.8:1 ratio: bp 98 °C (2 mmHg); UV (EtOH) λ_{max} 361 (ϵ 80); mass spectrum, m/z (relative intensity) 144 (5), 115 (16), 98 (19), 84 (54), 70 (30), 59 (100), 43 (28), 30 (21); NMR ($CDCl_3$) δ 0.99 (t, 0.8 H), δ 1.06 (t, 2.2 H, CH_3, *E* rotamer), 1.59 (d, 0.8 H, CH_3, *Z* rotamer), 2.0–2.42 (m, 2 H), 3.8–4.1 (m, 2 H), 4.46 (sextet, 0.74 H), 4.84 (sextet, 0.26 H), 5.28 (q, 0.26 H, OCHN, *Z* rotamer), 5.54 (t, 0.74 H, *E* rotamer).

Anal. Calcd for $C_6H_{12}N_2O_2$: C, 49.98; H, 8.39; N, 19.43. Found: C, 49.94; H, 8.49; N, 19.64.

Deamination of 1-Aminopropanol (14). After a 0.5 M aqueous solution of 500 mg (6.67 mmol) of 1-amino-2-propanol (**14**) had been adjusted to pH 5 by the addition of 0.6 mL (10 mmol) of glacial acetic acid, 5.6 mL (20 mmol) of 3.6 M aqueous sodium nitrite was added, and the mixture was stirred at 25 °C for 2 h. The reaction mixture was made basic by the addition of sodium carbonate and then extracted with methylene chloride. The solution was washed with 5% hydrochloric acid and dried over anhydrous potassium carbonate. Evaporation of the solvent gave 120 mg of a yellow oil. GLC analysis indicated that two compounds were present in a 24:1 ratio. The major component was *N*-nitroso-2-ethyl-1,3-tetrahydrooxazine (**16**, 12% yield), and the minor one was *N*-nitroso-1,3-tetrahydrooxazine (**15**, 0.6% yield). The two products were identical with authentic samples of **15** and **16**.

Preparation of an Authentic Sample of *N*-Nitroso-2-ethyl-1,3-tetrahydrooxazine (16). This compound was prepared as described by Eiter et al.[5] in 90% yield: bp 56 °C (0.4 mmHg) [lit.[5] bp 70 °C (0.3 mmHg)]; UV (EtOH) λ_{max} 364 (ϵ 86); IR (film) 2970, 2940, 2870, 1460, 1435, 1400, 1356, 1330, 1205, 1050 cm^{-1}; NMR ($CDCl_3$) δ 1.07 (t, 3 H), 1.72 (m, 2 H), 2.21 (m, 2 H, CH_2CH_3), 3.26 (m, 1 H, syn α axial at C-4), 4.54 (m, 1 H, syn α equatorial at C-4), 3.68–δ 4.24 (m, 2 H, OCH_2), 5.23 (t, 0.9 H, anti equatorial at C-2), 5,86 (t, 0.1 H, syn equatorial); mass spectrum, m/z (relative intensity) 144 (12), 115 (56), 85 (34), 84 (20), 71 (97), 59 (43), 57 (75), 56 (40), 42 (100), 30 (36).

***N*-Nitroso-2-ethyl-1,3-tetrahydrooxazine-*4,4-d*₂ (17).** H–D exchange of **16** was carried out as described previously: NMR ($CDCl_3$) δ 1.08 (t, 3 H), 1.70 (m, 2 H), 2.23 (m, 2 H), 3.7–4.41 (m, 2 H, OCH_2), 5.24 (t, 0.9 H, anti), 5.87 (t, 0.1 H, syn); mass spectrum, m/z (relative intensity) 146 (17), 117 (79), 88 (21), 87 (43), 73 (100), 59 (55), 57 (70), 44 (91), 30 (45).

***N*-Nitroso-1,3-tetrahydrooxazine (15).** This compound was prepared as described by Eiter et al.:[5] NMR ($CDCl_3$) δ 1.72 (sextet, 2 H), 3.96 (m, 2.7 H, α-CH_2 syn at C-4 and CH_2 (C-6)), 4.44 (t, 0.3 H, anti α-CH_2 (C-4)), 5.08 (s, 0.3 H, syn), 5.42 (s, 1.7 H).

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Registry No. 4, 39884-53-2; **5**, 77400-43-2; **6**, 124-68-5; **7**, 39884-58-7; **8**, 78-96-6; **9a**, 77400-44-3; **9b**, 77400-45-4; **10**, 77400-46-5; *trans*-**11**, 77400-47-6; *cis*-**11**, 77416-64-9; **12**·HCl, 17016-92-1; **13**, 77400-48-7; **14**, 156-87-6; **15**, 35627-29-3; **16**, 24033-81-6; **17**, 77400-49-8; ethanolamine, 141-43-5; propionaldehyde, 123-38-6; acetone, 67-64-1; acetaldehyde, 75-07-0.

Heterogeneous Catalysis in Organic Chemistry: Effect of Hydrogen Presaturation of the Catalyst in the Hydrogenation of Olefins

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A "time-lapse" procedure has been used to investigate the first few turnovers occurring in the hydrogenation of a double bond. Initial exposure of a platinum catalyst to either hydrogen or an olefin made no difference in the outcome of the reaction but initial treatment of a palladium catalyst with an olefin resulted in a change in its reaction characteristics. Presaturation of either the platinum or palladium catalysts with hydrogen results in the storage of a relatively large amount of hydrogen in the support by the process of spillover. By reverse spillover this hydrogen can migrate to the active sites on the catalyst and, thus, be available for reaction in the event that the site does not acquire hydrogen from the reaction medium rapidly enough.

The most common synthetic application of heterogeneous catalysis is in the hydrogenation of organic functional groups. For the most part, though, the conditions under which these hydrogenations are run are not based on any real understanding of the processes taking place on the catalyst surface. Instead, they are the result of empirical trial and error studies, or, more frequently, of conditions reportedly successful for similar reactions, or

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of the generalizations made in the books and reviews[1] dealing with the synthetic applications of hydrogenation. If more were known about the details of the interactions taking place on the catalyst surface and the influence which the reaction parameters have on these interactions, the selection of the optimal reaction conditions for a specific hydrogenation could be made with more certainty.

Most previous studies concerned with the details of the hydrogenation process have relied on the determination of rates of hydrogen uptake and/or product compositions from reactions run in a continuous gas flow over the catalyst or in a liquid suspension of the catalyst with the reactants present in amounts much greater than the number of active sites on the catalyst. As a result, even when these reactions were examined at low conversions, a large number of molecules have already reacted on each of the reaction sites of the catalyst. Further, the number of turnovers per site would be dependent on the relative reactivity of the different sites present on the catalyst. Thus, parameter effects, particularly the more subtle ones, could be masked by these kinetic factors and made even more indistinct if diffusion factors are present.[2]

It was considered, though, that detailed knowledge of a catalytic reaction would be obtained if the reaction could be slowed down sufficiently to permit an examination in, effectively, a stepwise manner. To accomplish this, one would first saturate the catalyst surface with one of the reactants, and the excess of this material would then be removed, leaving only that which was adsorbed on the catalyst. Introduction of the second reactant would then lead to a single reaction taking place at each of the occupied sites. Since no excess of the first reactant would be present, each site would react only once, eliminating the relative reactivities of the different sites and diffusion factors from consideration. In this way the product composition could be considered a reasonable determination of what was taking place on all of the active sites. With such a "time-lapse" approach the products obtained from a catalytic reaction could be examined one turnover at a time. That such an approach can be useful in looking at surface interactions was shown by the obtaining of decisive data on the hydrogenation of carbon monoxide with a system in which the catalyst was exposed to alternate pulses of CO and H_2.[3]

In order to determine whether such an approach could be used to examine the details of a catalytic hydrogenation, we felt that the reaction parameter examined first should be one which could readily be duplicated in both a classical solution-phase reaction and a vapor-phase, time-lapse, pulse reaction sequence. One such a parameter is the presaturation of the catalyst with hydrogen before the introduction of the substrate to be hydrogenated. While most mechanistic studies are run on hydrogen-presaturated catalysts, it is common in synthetic hydrogenations that the catalyst is not presaturated but, instead, is mixed with the substrate before exposure to hydrogen. We have found over the years, however, a number of instances in which the reaction rate and even the nature of the product were influenced by the status of the catalyst before the introduction of the substrate. For instance, in the palladium-catalyzed hydrogenation of $\Delta^{1,9}$-octal-2-one in dilute acid, more of the *cis-β*-decalone was formed over a nonpresaturated catalyst than was produced when the catalyst suspension was stirred under hydrogen for 20 min before the addition of the octalone. Further, while the rate of hydrogen uptake and the product composition were both constant over the entire reaction when a presaturated catalyst was used, both the rate and the product isomer ratio changed as the reaction proceeded over a nonpresaturated catalyst.[4] Even though such a difference was not always observed, at the very least those reactions in which the catalyst came in contact with the substrate before the hydrogen had an induction period (Figure 1).

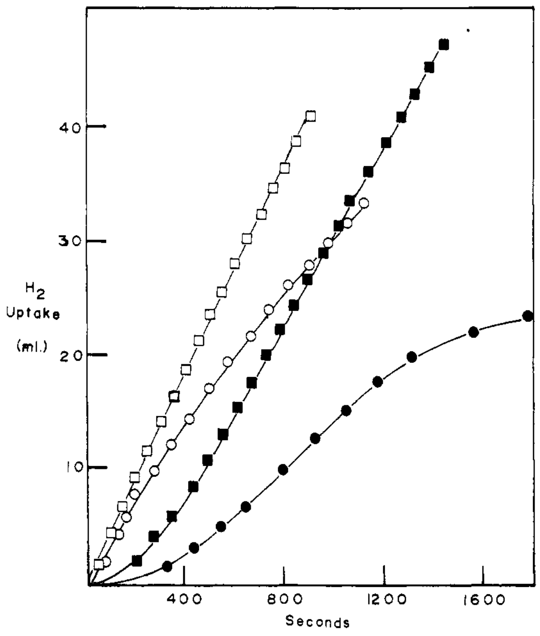
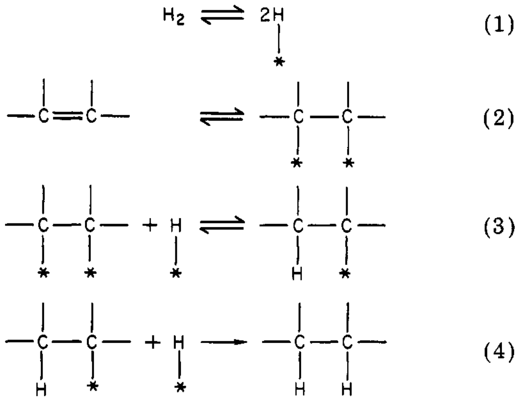


Figure 1. Rate of hydrogen uptake in olefin hydrogenation over presaturated and nonpresaturated platinum and palladium catalysts: 1-pentene over Pt-A; □ presaturated, ■ nonpresaturated; 1-pentene over Pd-A; ○ presaturated, ● nonpresaturated.

Scheme I



Consideration of the Horiuti–Polanyi mechanism for olefin hydrogenation (Scheme I) makes it difficult to see how this reaction would be influenced by the introduction of the olefin before the hydrogen or the reverse. It is

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(1) Augustine, R. L. "Catalytic Hydrogenation, Techniques and Applications in Organic Synthesis"; Marcel Dekker: New York, 1965. (b) Augustine, R. L. In "Organic Reactions in Steroid Chemistry"; Freid, J., Edwards, J., Eds.; Van Nostrand-Reinhold: New York, 1972; Vol. 1. (c) Augustine, R. L. *Catal. Rev.* **1976**, *13*, 285. (d) Freifelder, M. "Practical Catalytic Hydrogenation"; Wiley-Interscience: New York, 1971. (e) Freifelder, M. "Catalytic Hydrogenation in Organic Synthesis—Procedures and Commentary"; Wiley-Interscience: New York, 1978. (f) Kieboom, A. P. G.; Van Rantwijk, F. "Hydrogenation and Hydrogenolysis in Synthetic Organic Chemistry"; Delft University Press: Delft, The Netherlands; 1977. (g) Marvell, E. N.; Li, T. *Synthesis* **1973**, 457. (h) Rylander, P. N. "Catalytic Hydrogenation over Platinum Metals"; Academic Press: New York, 1967. (i) Rylander, P. N. "Catalytic Hydrogenation in Organic Synthesis"; Academic Press: New York, 1979.

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(4) Migliorini, D. C. Ph.D. Dissertation, Seton Hall University, 1966.

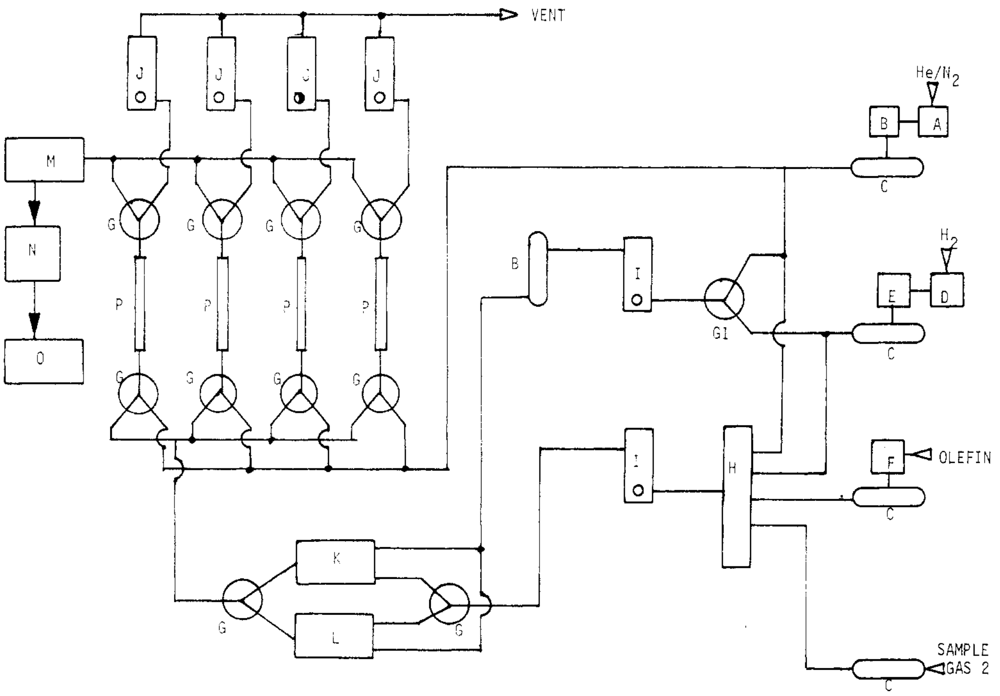

Figure 2. Apparatus for time-lapse study of catalytic reactions: A, Ridox column; B, indicating oxytrap; C, Matheson Model 450 purifier and Model 6183 filter; D, Engelhard Deoxo; E, Drierite column; F, alumina column; G, three-way valves; H, five-way valve; I, Rotameters; *J*, purgemeters; K, 10-μL Carle sampling valve; L, 50-μL Carle sampling valve; M, thermal-conductivity gas chromatograph; N, A/D converter; O, PET microcomputer; P, reactor tubes.

Table I. Product Composition on Hydrogenation of 1-Pentene to 4–5% Completion over Presaturated and Nonpresaturated Platinum and Palladium Catalysts

	% yield			
catalyst[a]	pentane	*cis*-2-pentene	*trans*-2-pentene	1-pentene
4.9% Pt/CPG-N	4			96
4.9% Pt/CPG-S	5		3	92
1.8% Pd/CPG-N	4	9	17	70
1.8% Pd/CPG-S	5	8	12	75

[a] N = nonpresaturated and S = presaturated.

possible that during that hydrogen saturation step species adsorbed on the catalyst are removed making it more reactive. Another possibility is that the initial adsorption of the olefin could modify the catalyst surface and, thus, change its reaction characteristics.

When the liquid-phase hydrogenations of 1-pentene over presaturated and nonpresaturated platinum and palladium catalysts were stopped at 3–5% completion, the product compositions listed in Table I were obtained. These data show that about the only difference with catalyst pretreatment is the somewhat greater extent of isomerization with the nonpresaturated palladium catalyst as compared with the products obtained with hydrogen-saturated palladium. This was not unexpected given the facile isomerization ability of palladium[1] and the longer contact time of the olefin with the nonpresaturated catalyst (Figure 1).

From these product compositions and the hydrogen uptake data in Figure 1 it would be difficult to determine why the specific catalyst pretreatment used would have an influence on the reaction. One reason for this is the fact that even this low conversion corresponds to about 20–30 turnovers per "active site" if every metal atom is considered to be such a site. This assumption, though, is erroneous because a reasonable percentage of the metal atoms are in the interior of the supported metal particles, and, most probably, all surface atoms are not reactive. Thus, the number of turnovers per active site is more likely in the region of 100 or even more, and anything which might have taken place on the catalyst surface at the beginning of the reaction would, most likely, be obscured.

It was considered, then, that the effect of catalyst presaturation on olefin hydrogenation would more readily be studied by using a time-lapse approach. Further, the amount of detailed information obtained from this investigation would be an indication of the success which this approach could have in examination of other catalytic reactions.

Experimental Section

The hydrogen used was commercial grade purified by passage through, successively, an Engelhard Deoxo unit, a Drierite trap, a Matheson Model 450 gas purifier, and a Matheson Model 6183 high-purity filter. The helium and nitrogen were Zero Grade, 99.9995% pure, and were further treated by passage through a 30 × 0.8 cm column of Ridox (Fischer Scientific), two 30 × 0.8 cm columns of indicating Oxy-Trap (Altech Associates), a Model 450 gas purifier, and a Model 6183 filter. From the specifications provided for these oxygen traps it was estimated that the oxygen level in these carrier gases was less than 1 ppm on passage through the reactor. The 1-butene was 99.0% pure and was passed through a 50 × 0.4 cm column of alumina, a Model 450 purifier, and Model 6183 filter before use. The Controlled Pore Glass (CPG, Electronucleonics, Inc.) was 80–120 mesh with a mean pore diameter of 116 Å, a pore size distribution of ±8.6%, a pore volume of 0.78 cm^3/g, and a surface area of 155 m^2/g. It was purified[5] by refluxing for 48 h in a 1:1 mixture of concentrated HCl and concentrated HNO$_3$. It was then washed with triple-distilled water and refluxed in a Soxhlet extractor for 48 h with a saturated solution of Ca(OH)$_2$ in triple-distilled water. After being dried at 110 °C, it was then heated to 500 °C in a 30-cm^3/min stream of oxygen.

A diagram of the apparatus used is shown in Figure 2. The carrier gas flow was monitored by using a calibrated Matheson 7630 150-mm Rotameter. The pulses of the reactant gases could be injected into the carrier gas stream by either a 10- or a 50-μL

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(5) Vanderspurt, T. H. In "Catalysis in Organic Synthesis"; Jones, W. H., Ed.; Academic Press: New York, 1980; p 11.

purged Carle six-port sampling valve. The reactors used were 25-cm lengths of 6-mm o.d. Pyrex tubing indented near the center to keep the catalyst from blowing through. The catalyst sample was held in place between two plugs of calcined Pyrex glass wool. The four parallel reactors permitted the facile examination of several catalyst samples without the necessity of changing reactor tubes. All valves and fittings were gas tight as shown by the passage of a 30-cm^3/min flow of the deoxygenated carrier gas through the entire system and through a column of indicating Oxy-Trap placed in the vent line for 24 h with no change in the color of the Oxy-Trap. The presence of a leak could readily be detected by this procedure.

The reaction products were analyzed by gas chromatography through an 8 ft × $^1/_8$ in. stainless-steel column of 0.19% picric acid on GP-80-100 Carbopac C with both the column and the TC detector at ambient temperature. The output of the detector was passed both to a recorder and through an A/D converter to a 2001 Commadore PET microcomputer for data acquisition and evaluation.[6] Detection limits of this system were 0.1–0.2 μL of gaseous hydrocarbon. The values reported are corrected for the different relative response factors for butane and the butenes as determined by calibration with samples of each of the butenes and butane. Retention times at a flow of 30 cm^3/min were as follows: 1-butene, 12 min; butane, 14.5 min; *cis*-2-butene, 16.25 min; *trans*-2-butene, 19.25 min.

Turnover Procedures. The catalyst (5 mg) was placed between two plugs of calcined Pyrex glass wool in a reactor tube and connected to the system. Helium was passed through the reactor for 1–2 h to purge the system of air. If the catalyst were to be saturated with hydrogen, valve G1 was switched to permit a hydrogen flow over the catalyst. Otherwise, valve H was used to select which gas, H_2 or 1-butene, would be pulsed into the carrier gas through the sampling valve K. If the catalyst were to be exposed to the olefin first, several 10-μL pulses of 1-butene were passed over the catalyst, and the amount adsorbed was determined by GC analysis of the effluent gas since after the first 1 or 2 pulses the detector response is constant for each 10-μL unit and calculation of how much material was present from the initial pulses after contact with the catalyst is routine. The normal turnover sequence was comprised of three 10-μL pulses: H_2, 1-butene, H_2. Prolonged turnovers required the following sequence: H_2, 1-butene, H_2; H_2, 1-butene, H_2; H_2, 1-butene, H_2; etc. After the 1-butene pulse the products were analyzed by GC. The second H_2 pulse follows this analysis. The timing of the first H_2 pulse and the 1-butene pulse was such that there was no overlap of the products formed from these pulses in the GC. The limit of detection with the system is between 0.1 and 0.2 μL of hydrocarbon or between 1% and 2% of the 10-μL pulse.

Reverse-spillover pulsed olefin titration was accomplished by passage of 10-μL pulses of 1-butene over a 5-mg sample of presaturated catalyst. Since only 1-butene and butane were present in the effluent gases with platinum catalysts, a 3.5-min interval between pulses at 30 cm^3/min was used. Over Pd a 9-min interval was used.

Catalyst Preparation. The 4.9% Pt/CPG[7] (Pt-A) was prepared by heating a 0.2 M solution of H_2PtCl_6 in 1:1 NH_4OH–H_2O at 90 °C until the odor of NH_3 was faint, diluting this solution to 150 mL with triple-distilled water, and adding this at a rate of 12 drops/min to a suspension of 10 g of purified CPG in aqueous NH_4OH (pH 11) at 75 °C with slow stirring. After the addition was completed, the mixture was stirred an additional 20 min at 70 °C. The solid was separated by filtration and washed with three 200-mL portions of triple-distilled water. After the solid was dried overnight at 110 °C a yellow material was obtained which was reduced in a 30 cm^3/min stream of hydrogen at 200 °C for 2 h and then cooled to room temperature under nitrogen. The catalyst was stored in a screw-capped bottle in air for at least 3–4 weeks before use.

The 1.6% Pd/CPG (Pd-A) catalyst was prepared in essentially the same way by substituting $PdCl_2$ for the H_2PtCl_6. The more reactive catalysts, 4.3% Pt/CPG (Pt-B) and 1.8% Pd/CPG (Pd-B), were prepared by using a more rapid stirring and slower addition rate.

Liquid-phase hydrogenations were run in a jacketed 50-mL reaction flask[8a] on a sloping manifold apparatus[8b] as previously described[9] with 25 mg of catalyst, 20 mL of heptane, and 0.25 mL of olefin. In the nonpresaturated runs the saturation step was eliminated, and the olefin, solvent, and catalyst were placed in the reaction flask before it was evacuated and filled with hydrogen. The heptane was purified by hydrogenation over 5% Pd/C for 10–12 h and distilled from sodium immediately before use. The olefins were passed through a column of alumina prior to use.

Results and Discussion

The catalysts used in this study were selected to provide the special characteristics thought to be advantageous in establishing the basic conditions needed for a time-lapse study of an olefin hydrogenation. Platinum and palladium were used since they are the noble metals most commonly used to catalyze the addition of hydrogen to double bonds.[1] Controlled Pore Glass (CPG) was chosen as the support material for several reasons. Preliminary work indicated that the common supports, carbon, silica, and alumina, could promote olefin isomerization and/or absorb some of the reaction products. CPG was found to do neither. Further, the presence of large, uniformly sized pores in this material would mean that all of the supported metal particles would be readily accessible to the reactants, and the results obtained would not be overshadowed by any pore-diffusion parameters.[5] The preparation procedure was varied to provide pairs of catalysts having essentially the same quantity of supported metal but different activities.

For a closer parallel to the conditions commonly used in synthetic applications of catalytic hydrogenations, the catalysts, after reduction of the metal salts on the support, were left exposed to air for 3–4 weeks before use, and no special pretreatment of the catalyst was used prior to its exposure in the reactor to either hydrogen or 1-butene at ambient temperature.

Preliminary studies to determine the viability of this time-lapse approach were run by using 5-mg portions of a 4.9% Pt/CPG catalyst (Pt-A). The catalyst was exposed first to a 10-μL pulse of hydrogen followed by a 10-μL pulse of 1-butene. The products formed were analyzed by an on-stream thermal conductivity gas chromatograph. Virtually no tailing of the peaks was observed, indicating that reactions had taken place rapidly on the surface and that there was no gradual removal of any hydrocarbon from the catalyst. The amount of butane formed corresponded to 44% of the 1-butene passed through the reactor. About 3% of this olefin was isomerized to a mixture of *cis*- and *trans*-2-butenes, 43% was unchanged, and about 10% remained on the catalyst. Passing a 10-μL pulse of hydrogen over the catalyst resulted in the saturation of this material to form butane. The product compositions from the initial turnovers on this and other catalysts are given in Table II. Succeeding turnovers were accomplished by the successive passage of a 10-μL pulse of hydrogen to saturate the catalyst surface with hydrogen, a 10-μL pulse of 1-butene to react, and, finally, another 10-μL pulse of hydrogen to saturate the adsorbed olefin and complete the turnover. On a continuing basis this corresponded to the following sequence of pulses: H_2, olefin, H_2; H_2, olefin, H_2; H_2, olefin H_2; etc. After three turnovers the product composition reached a set level which then remained constant for all succeeding turnovers. This constant product composition was 69% of the 1-

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(6) Ashworth, H. A.; Augustine, R. L. *Rev. Sci. Instrum.* **1981**, *52*, 57.

(7) Analyses were run by Schwarzkopf Microanalytical Laboratory.

(8) (a) Reference 1a, p 20. (b) Reference 1a, p 12.

(9) Augustine, R. L.; Migliorini, D. C.; Foscante, R. E.; Sodano, C. S.; Sisbarro, M. J. *J. Org. Chem.* **1969**, *34*, 1075.

Table II. Composition of Products Obtained in Time-Lapse Study of the Hydrogenation of 1-Butene[a]

		initial turnover, %					constant values, %			
catalyst	first reactant[b]	butane	2-butenes[c]	olefin on catalyst[d]	1-butene	turnovers[e]	butane	2-butenes[c]	olefin on catalyst[d]	1-butene
Pt-A	H_2	44	3	10	43	3	18	4	9	69
	ene	23	3-4	9	64	3	18	4	9	69
Pt-B	H_2	14	3-4	30	52	4	59	4	30	6
	ene	53	3-4	27	16	4	59	4	30	6
Pd-A	H_2	7	86		7	4	27	70		3
	ene	6	84	4	6	10	20	63	13	4
Pd-B	H_2	20	76		3	8	54	45		
	ene	7	76	4	12	7	20	68	8	4

[a] 10-μL pulses of 1-butene, 30 cm^3/min carrier gas flow, 3.5 min between reactant pulses. [b] First reactant to come in contact with the catalyst; ene = 1-butene. [c] Mixture of cis and trans isomers. [d] Converted to butane by second H_2 pulse. [e] Number of turnovers to a constant value.

butene unchanged, 4% isomerized, 18% saturated, and 9% remaining on the catalyst to be saturated by the second hydrogen pulse. The constant-value product data for the different catalysts studied are also listed in Tabe II.

Since there was an occasional production of a small amount of butane by the first hydrogen pulse of later turnovers, it was necessary to have a several minute delay between the introduction of this hydrogen and the 1-butene pulse to permit chromatographic separation of this small butane peak from the normal turnover analyses. Because of this delay it was thought that some of the initially adsorbed hydrogen might have been swept off the catalyst by the carrier gas stream before the olefin was introduced. To determine if this were occurring, we first subjected the catalyst to several turnovers to reach a constant product composition and then both the carrier gas flow and the time between the reactant pulses were varied for succeeding turnovers. The data obtained are depicted in Figure 3. These results show that an appreciable amount of the hydrogen on the catalyst can be removed by the carrier gas before the olefin reaches the reactor. The faster the flow the more rapid the removal. There is, however, a leveling at about 13% butane formation observed with the two faster flow rates. Presumably, the results from the slowest flow would also show this if the time interval between pulses were long enough. Care must be taken in this regard, though, since it is possible to remove essentially all of the hydrogen from the catalyst by exposure to a carrier gas flow for 12–15 h.

It can be seen from the data in Figure 3 that if the amount of saturated product formed from these reactions is extrapolated to zero time between reactant pulses, about 21–22% butane formation would occur, regardless of the flow rate. This value and the previously mentioned leveling at about 13% butane formation indicate that about one-third of the reactive hydrogen on the surface of this catalyst is less strongly adsorbed than the remaining two-thirds.

The amount of butane formed from reaction of the second hydrogen pulse with the olefin remaining on the catalyst stays relatively constant regardless of the amount of hydrogen swept off prior to the introduction of the 1-butene. If a second 10-μL pulse of 1-butene were passed over the catalyst before the second hydrogen pulse, all of this olefin goes through the reactor unchanged. Addition of hydrogen then still gives the same amount of butane, so the second olefin pulse had no effect on the reaction. Further, if larger pulses of 1-butene were used in the turnover sequence, the absolute amounts of butane and the 2-butenes formed remain the same as does the amount of olefin remaining on the catalyst. The excess 1-butene goes through the reactor unchanged. Thus, the contact time of the olefin with the catalyst is not a factor in this turnover sequence. These data were reproduced over several samples of the Pt-A catalyst. Because of the similarity of the extrapolated data from each flow rate, all further work was done at a single carrier gas flow rate, the experimentally most convenient (30 cm^3/min).

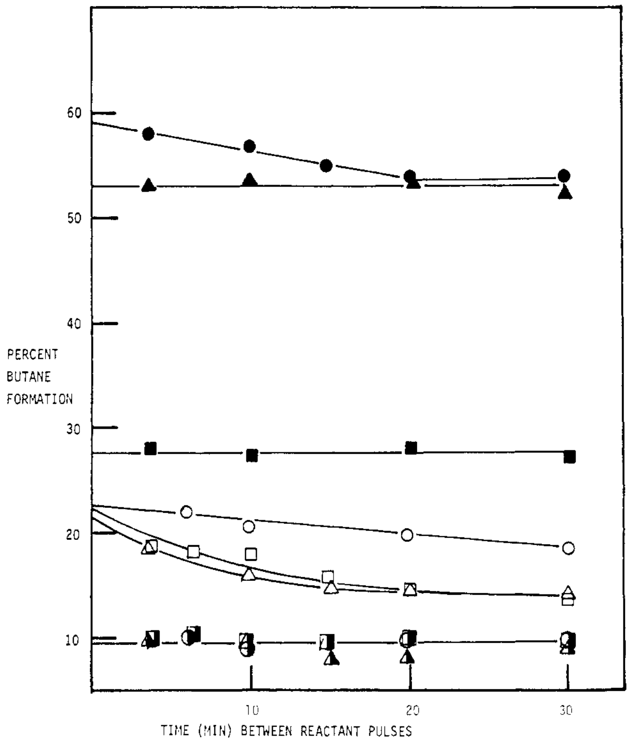

Figure 3. Extent of hydrogen sweep off before olefin pulse in a time-lapse study. Amount of butane formed after 1-butene pulse: ○, Pt-A, 15 cm^3/min carrier gas flow; □, Pt-A, 30 cm^3/min carrier gas flow; △, Pt-A, 50 cm^3/min carrier gas flow; ●, Pt-B, 30 cm$_3$/min carrier gas flow; ■, Pd-A, 30 cm^3/min carrier gas flow; ▲, Pd-B, 30 cm^3/min carrier gas flow. Amount of butane formed after second hydrogen pulse: Pt-A, ◑, 15 cm^3/min carrier gas flow; half-solid box, 30 cm^3/min carrier gas flow; half-solid triangle, 50 cm^3/min carrier gas flow.

A 4.3% Pt/CPG (Pt-B) catalyst was prepared under conditions expected to give a more active catalyst than Pt-A. This expectation was verified by the obtaining of about 3 times as much saturation per turnover as produced by Pt-A. As shown in Table II, after completion of four or more turnovers, Pt-B converted a 10-μL pulse of 1-butene to 59% butane and 4% 2-butene, with 30% remaining on the catalyst. The use of a larger pulse of 1-butene again resulted in the formation of the same absolute amounts of saturation, isomerization, and adsorption, with the excess going through the reactor unchanged. As with the Pt-A, some hydrogen was also removed from

Table III. Product Composition on Successive Turnovers on Pd-B

	H_2 first[a]				olefin first[b]				
turnover no.	% butane	% *cis*-2-butene	% *trans*-2-butene	% 1-butene	% butane	% *cis*-2-butene	% *trans*-2-butene	% Ads[c] 1-butene	% 1-butene[c]
1	20	26	51	3	7	34	43	4	12
2	36	21	41	2	11	28	49	6	6
3	41	17	38	3	14	24	48	8	5
4	44	17	37	2	15	21	51	8	5
5	47	16	34	2	17	21	48	8	5
6	51	15	34		17	20	51	8	4
7	54	14	31		20	20	47	9	4
8	54	14	31		20	20	47	9	4
9	54	14	31		20	20	47	9	4

[a] Surface of the catalyst first saturated with H_2. [b] Surface of the catalyst exposed first to a pulse of a butene followed by the standard turnover sequence. [c] Removed as butane by a second hydrogen pulse.

Pt-B between the introduction of the first hydrogen pulse and the olefin. The data in Figure 3 show, however, that only about 7% of the reactive hydrogen on this catalyst is easily removed in contrast to the 33% from Pt-A.

Two Pd/CPG catalysts of differing activities were also studied. The 1.6% Pd/CPG (PD-A) catalyst gave on the first turnover only a 7% conversion to butane, but 86% of the 2-butene isomers was produced with a cis/trans ratio of 0.79. After the fourth turnover the product composition leveled off at 27% butane, 3% unreacted 1-butene, and 70% 2-butene with a cis/trans ratio of 0.43 (Table II). The facile isomerization ability of the palladium catalyst[1] was further illustrated by the fact that when the size of the 1-butene pulse was doubled, the absolute amount of the butane formed remained the same, but all but 3% of the remaining 1-butene was isomerized. In addition to this extensive isomerization, Pd-A was also different from the platinum catalysts in that no olefin was retained on the catalyst to react with the second hydrogen pulse. Further, varying the time between the pulses of reactants had no effect on the product composition (Figure 3). Thus, none of the reactive hydrogen on the surface of this catalyst was readily removed by the carrier gas during the time span investigated.

The Pd-B catalyst (1.8% Pd/CPG) also showed these same isomerization characteristics, strong adsorption of hydrogen, and lack of olefin adsorption. But, in contrast to the other catalysts, the product composition changes observed with sucessive turnovers were more gradual (Table II and III). That Pd-B was more reactive than Pd-A can be seen from the data in Table II, showing twice as much saturation taking place over Pd-B than over Pd-A.

All of these results show that a "time lapse" approach can be used to provide detailed information about the initial stages of an olefin hydrogenation. The turnover sequences described, however, were not typical of common synthetic hydrogenations. As mentioned previously, the usual procedure is to mix the catalyst with the substrate before the introduction of the hydrogen rather than the reverse sequence used in these initial trials. According to the Horiuti–Polanyi mechanism (Scheme I), though, it should make no difference which reactant was adsorbed on the catalyst first unless one of them can modify the surface and, thus, change the reaction characteristics of the catalyst. To determine if this could be taking place, we first exposed each of the four catalysts described above to several 10-μL pulses of 1-butene. Only Pd-B adsorbed a detectable amount (0.5 μL) of olefin. Pt-B adsorbed possibly a trace, but no adsorption could be discerned with Pt-A and Pd-A. This olefin pretreatment was then followed by the standard turnover sequence: hydrogen, olefin, hydrogen. The product compositions found from the first turnovers and after constant values were obtained are listed in Table II.

After three or four turnovers the reaction products obtained with the platinum catalysts were the same as those found when the catalyst was treated first with hydrogen. With these catalysts, then, substrate modification of the surface probably does not occur because, as discussed below for the palladium catalysts, such a modification can be produced by even very small amounts of olefin on the catalyst. Thus, the induction period observed with the nonpresaturated platinum catalyst in solution (Figure 1) is most likely due simply to the removal of adsorbed oxygen. The parallel hydrogen uptake shown in Figure 1 for the presaturated platinum catalyst and the nonpresaturated species supports this conclusion.

Extensive isomerization was again observed over the palladium catalyst (Table II), and the changes in product composition with sucessive turnovers were more gradual (Table III). But with these catalysts marked differences in product compositions were observed, depending on whether the catalyst was exposed to hydrogen or the olefin first. The most dramatic difference can be seen in the data listed in Table II for Pd-B on which the most olefin was adsorbed in the pretreatment step. It seems likely that this adsorption resulted in a modification of this catalyst because there was no further change in product composition from that shown in Tables II and III even after several more turnovers. This modification resulted not only in the formation of considerably less butane than observed previously but also in the presence of a reactive butene on the catalyst which is saturated by the second hydrogen pulse of the turnover sequence. This behavior was typical of the platinum catalysts but not of the palladium catalysts exposed first to hydrogen.

A similar but less dramatic change in product composition was noted with the Pd-A catalyst even though the adsorption of 1-butene in the pretreatment stage was not detectable. It appears, then, that whatever the nature of this catalyst modification, it can be accomplished by very small amounts of olefin. The marked discrepancy in the hydrogen uptake curves of the presaturated and nonpresaturated palladium catalysts is further evidence of the difference between these two catalysts. Obviously, further work is needed to develop a better understanding of what the olefin does to the catalyst surface and why it does not take place when hydrogen is present.

There still remains the matter of what is taking place over a hydrogen-presaturated catalyst. The initial work describing what was occurring on a catalyst that has been initially exposed to a pulse of hydrogen may be meaningful, but normally the presaturation of a catalyst is accomplished by exposure to a hydrogen atmosphere for a period,

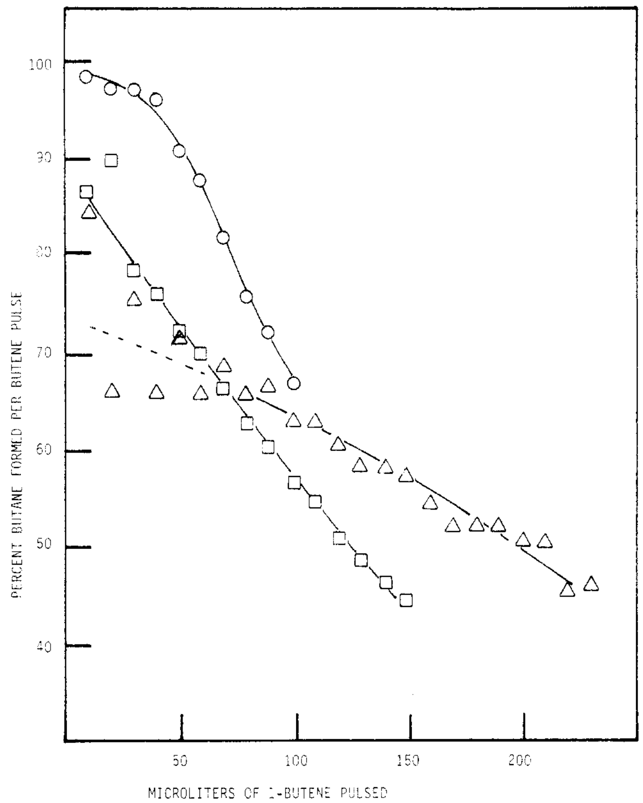

Figure 4. Effect of flow rate of partial reverse spillover pulsed olefin titrations: run on 5 mg of Pt-A; H_2 presaturation at 30 cm^3/min for 60 min; both presaturation and olefin reactions run at ambient temperature; ○, 15 cm^3/min reactor flow; □, 30 cm^3/min reactor flow; △, 50 cm^3/min reactor flow.

usually, of 15–60 min. Generally, a considerable amount of hydrogen is absorbed by the catalyst during this procedure. For the reactions depicted in Figure 1, presaturation resulted in the uptake of between 1.5 and 2.5 mL of hydrogen by 25 mg of catalyst. It seemed, then, that a better parallel to this situation than simply covering the catalyst with a single pulse of hydrogen would be to expose it to a stream of hydrogen for a prolonged period of time and follow this with a normal turnover sequence.

When 5 mg of Pt-A was placed in a stream of hydrogen at ambient temperature for 60 min and then reacted with a 10-μL pulse of 1-butene in a carrier gas flow of 30 cm^3/min, almost 85% of the olefin was saturated; considerably more than was observed in any previous run. On continued pulsing of 10-μL samples of 1-butene with no further addition of hydrogen, decreasing but still extensive amounts of butane were formed. The 15th pulse was 40% saturated, with the rest of the 1-butene going through the reactor unchanged. No isomerization products were detected. As shown in Figure 4, repetition of this sequence with different carrier gas flows gave similar results. These data indicate extensive hydrogen storage in the catalyst system during the saturation step. At the lowest flow rate, butane formation was almost complete for the initial olefin pulses, while at the higher flows initial butane formation was somewhat lower and with the highest flow was rather erratic. These facts imply that the extent of olefin saturation is dependent on the time it is in contact with the catalyst. Similar results were also obtained from catalysts which were saturated for 12-20 h, so this catalyst was completely saturated with hydrogen in at least 60 min. A 15-min exposure to hydrogen, though, was not sufficient for complete saturation.

For the determination of the amount of hydrogen present in the saturated catalyst this pulsed olefin titration sequence was carried to completion with the results shown in Figure 5. From these data it can be determined that at least 6.2 μmol of hydrogen is present in this 5-mg portion of saturated Pt-A which contains only a total of 1.2 μmol of platinum, a H_2/Pt ratio of 5:1. Since it is highly unlikely that every platinum atom in the catalyst is on the surface of the metal particles[10] present on the support, the amount of hydrogen per surface platinum atom is probably much higher. A similar high 4:1 H_2/metal ratio was also found on presaturation of a number of catalysts in solution (Figure 1). There is no reasonable way in which this H_2/Pt ratio can be accounted for by simple adsorption on the metal surface.

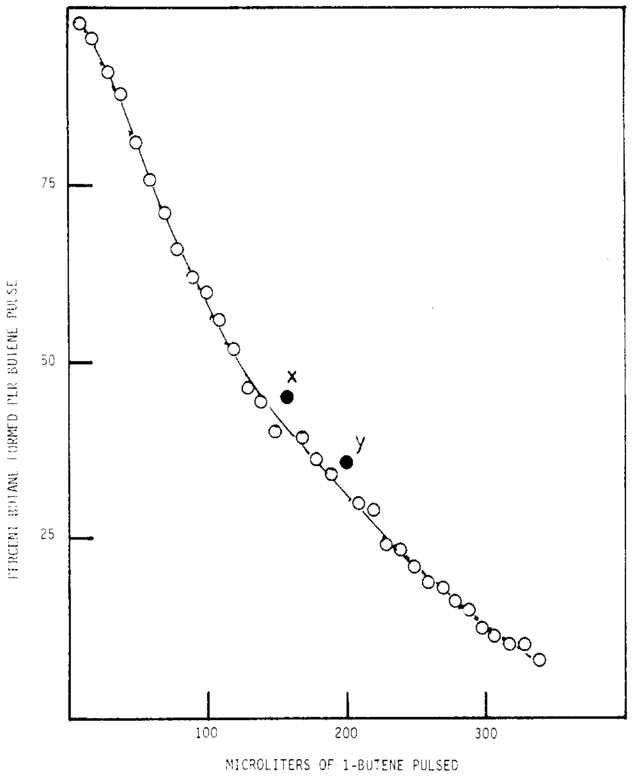

Figure 5. Complete reverse spillover pulsed olefin titration on 5 mg of Pt-A presaturated for 15 h at 30 cm^3/min, at a reactor flow rate of 15 cm^3/min, and with a 3.5-min interval between 10-μL 1-butene pulses, except for points x and y which were obtained after a 10- and 5-min interval, respectively.

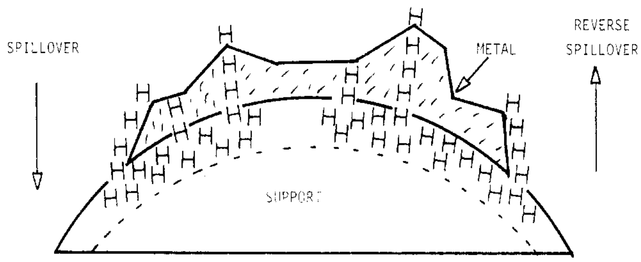

Figure 6. Hydrogen spillover and reverse spillover.

Rather, it would be more rational to consider the possibility of hydrogen spillover,[11-13] a process by which the metal particles of the catalyst promote "storage" of hydrogen in the support material itself. This adsorption of hydrogen does not occur without the intermediacy of a

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[10] For the ratio of surface atoms to bulk atoms in different crystalline shapes of varying size, see: Van Hardeveld, R.; Hartog, F. *Surf. Sci.* **1969**, *15*, 189.

[11] Sermon, P. A.; Bond, G. C. *Catal. Rev.* **1973**, *8*, 211. (1973); *J. Chem. Soc., Faraday Trans. 1*, **1976**, *72*, 745; **1980**, *76*, 889.

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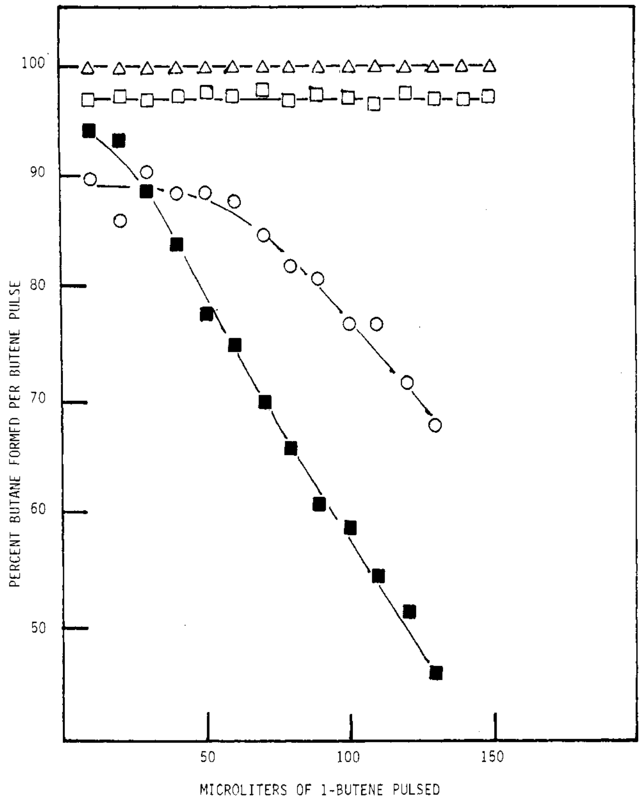

Figure 7. Partial reverse spillover pulsed olefin titrations: run on 5 mg of catalyst; H_2 presaturation at 30 cm^3/min for 19 h; reactor flow rate of 30 cm^3/min; both presaturation and olefin reactions run at ambient temperature; □, Pt-B; ○, Pd-A; △, Pd-B; ■ 1.5% Pt/SiO_2

catalytically active metal in physical contact with the support. Further, the process is reversible, and, as the reverse spillover pulsed olefin titration data in Figures 4 and 5 show, as the hydrogen is removed from the active sites by reaction with the olefin more hydrogen migrates to these sites from the spillover "reservoir". This process is depicted diagramatically in Figure 6.

The dependence of the amount of butane formed on the time of olefin contact with the catalyst shows that this reverse spillover takes time with this catalyst. The two points, x and y, in Figure 5 which are off the general curve represent data obtained after a 10- and 5-min delay, respectively, between butene pulses rather than the standard 3.5 min. The obtaining of somewhat more saturation in these two instances shows that the longer time between pulses permitted more hydrogen to migrate to the active sites on the metal, a further illustration of the time element associated with this reverse spillover.

These partial reverse spillover pulsed olefin titrations were extended to other catalysts which were first saturated by exposure to a stream of hydrogen for 19 h. The results obtained are also depicted in Figure 7. Pd-A and a 1.5% Pt/SiO_2 catalyst exhibited much the same behavior as did Pt-A. Pt-B and Pd-B, on the other hand, had such extensive spillover that even after reaction with 150 μL of butene complete conversion to butane was still taking place. With the palladium catalysts an additional factor, that of hydrogen absorption in the metal,[14] is also possible. The relative importance of this factor with respect to spillover cannot be ascertained from the data at hand.

Toward the end of the partial olefin titration sequence run on Pd-A, two 20-μL pulses of 1-butene were used to see if a contact time dependency existed with this catalyst as it did with Pt-A. In both instances the amount of butane formed was essentially that formed from a 10-μL pulse, thus pointing out another difference between these platinum and palladium catalysts. As expected, the product mixtures obtained from these saturated palladium–olefin titrations consisted only of butane and the isomerized olefins. No 1-butene was detected.

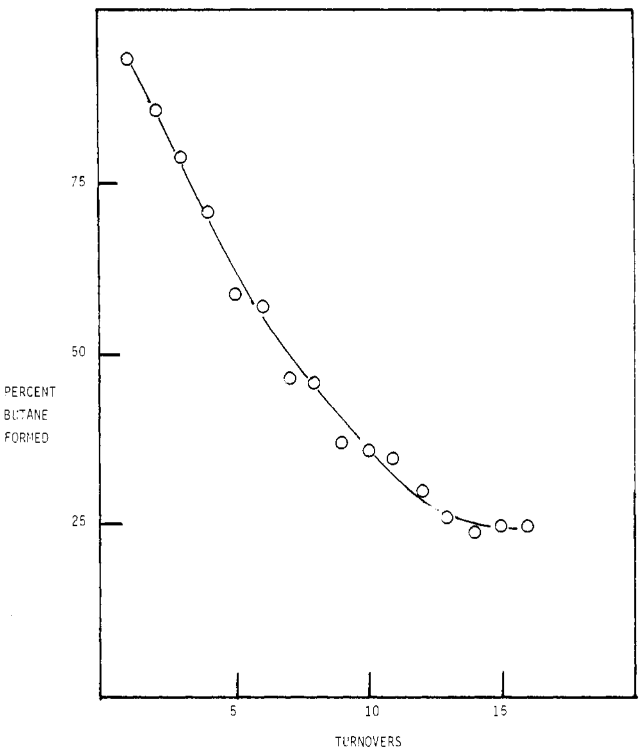

Figure 8. Effect of spillover on butane formation from turnover sequences run on 5 mg of hydrogen-saturated Pt-A.

For clarification of the effect of this spillover on olefin hydrogenation, a series of turnovers, as described above, were run on the presaturated Pt-A. The amount of butane formed from each of these turnovers is depicted in Figure 8. These data show a decrease in butane formation over the first 12 turnovers and then a leveling at a 24% conversion to butane. Again, no isomerized products were detected, and, as anticipated because of the presence of the "stored" hydrogen available to the active sites, no olefin was left on the catalyst. Thus, this reaction appears more straightfoward than those observed in previous turnover sequences. Presaturation of the catalyst results in the storage in the support material of a rather large amount of hydrogen which serves as a "reservoir" during the hydrogenation. When hydrogen is not available to an active site from the reaction medium because, for instance, of unfavorable diffusion factors,[2] reverse spillover can occur to keep these sites reactive. Evidently, in the very early stages of the reaction, diffusion of hydrogen to the active sites from the medium, spillover of excess adsorbed hydrogen, and reverse spillover to hydrogen deficient sites all balance to give a steady reaction rate. In contrast to what occurs over nonpresaturated catalyst, though, this process is more reactive in the initial turnovers, so no induction period is observed for the reaction.

Conclusions

The time-lapse technique described here has been shown to be effective in examining the details of the initial stages of the catalytic hydrogenation of an olefin. These details show that the differences commonly seen in the use of hydrogen saturated or nonsaturated catalysts in this re-

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action depend on the metal used to promote the reaction. With platinum the induction period observed with a nonpresaturated catalyst is probably due merely to the removal of adsorbed oxygen and not to any long term interaction of the olefin with the catalyst surface. Over palladium, if hydrogen is not present, reaction with even a very small amount of olefin results in a distinct change in the reaction characteristics of the catalyst as compared with what takes place if the catalyst is treated first with hydrogen. The data in Figure 1 for solution-phase hydrogenations are in agreement with these conclusions.

Presaturation of these catalysts with hydrogen results in the storage of relatively large amounts of hydrogen in the support material by the process of spillover. With these presaturated catalysts, reactions with olefins are more straightforward because of this hydrogen "reservoir" in intimate contact with the active sites. Here, too, there appear to be some differences between platinum and palladium. The reverse spillover to the metal particles of a supported palladium catalyst seems to be occurring at a slower rate than it does with similar platinum catalysts. This is indicated by the observation that there was virtually no contact time dependence on the amount of saturation taking place on an olefin pulse passing over a presaturated palladium catalyst while over a platinum catalyst the extent of saturation depends on the time the olefin pulse is in contact with the catalyst. This comparison is somewhat tenuous, though, and more work is obviously needed to determine the validity of this conclusion.

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Registry No. Pentane, 109-66-0; *cis*-2-pentene, 627-20-3; *trans*-2-pentene, 646-04-8; 1-pentene, 109-67-1; butane, 106-97-8; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; 1-butene, 106-98-9.

Reductive Cyclizations Involving Attack of Radical Anions Derived from Ketones, Aldehydes, and Enones on Isolated Carbon–Carbon Triple and Double Bonds. Application of Frontier Molecular Orbitals

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Reductive cyclization to tertiary alcohols was carried out with 4.5-secocholestan-5-one in which the 10α side chain was varied from $(CH_2)_2C{\equiv}CH$ (**1a**), to $(CH_2)_2C{\equiv}CCH_3$ (**1b**), $(CH_2)_3C{\equiv}CH$ (**1d**), and $(CH_2)_2CH{=}CH_2$ (**4**) by using $Na/NH_3/THF$ (method B) and Na/THF (method C), and the results were compared with those obtained previously by using $C_{10}H_8Na/THF$ (method A). Cyclization was the sole product with methods A and C but was accompanied by reduction to secondary alcohol when method B was used. Cyclization was regiospecific (formation of a smaller ring) and stereoselective (with only 5β-ol being produced). With **1b** initial syn attack by the ketyl radical anion across acetylene was further confirmed. The final product was predominantly the *E* isomer with methods A and B but the *Z* isomer with method C. Reductive cyclization was extended to 16,17-secopregn-5-enes whose side chains at 13α and 14β were varied, respectively, from $C{\equiv}CCH_3$ and CH_2CHO (**31**) to $C{\equiv}CCH_3$ and CH_2COCH_3 (**40**), $CH{=}CHCH_3$ and CH_2CHO (**44**), and $CH{=}CHCH_3$ and CH_2COCH_3 (**45**). Comparative studies were carried out and all products fully characterized except alkylnaphthalenes from **45**. Thus **31** gave a mixture of the four stereoisomers of 16-hydroxypregna-5,17(20)-dienes. This reaction was still regiospecific but no longer very stereoselective. The 16β-ols predominated as did the *Z* isomers. Results were markedly similar with all three methods, confirming the similarity in mechanisms. Rapid isomerization of vinyl radicals formed by syn addition is suggested. Method B gave no reduction products. From both **44** and **45** this method gave only two cyclized products differing in the configuration at position 16, with 16α-ols predominating. For an explaination of the lack of steric effect in replacement of the hydrogen of aldehyde by methyl on the 16α/16β raios an FMO argument has been advanced which uses an SOMO–HOMO interaction between radical and olefin instead of the presently accepted SOMO–LUMO for radical cyclizations. Application of FMO methods was justified by showing that 7α-methyl substitution in **1a** does not prevent C–C bond formation at the 5α-position. Stereoselective formation of the equatorial 5β-ols in these cases is ascribed to a dissymetric FMO for the ketyl radical ion, with the orbital at C-5 being extended in the axial direction. Reductive cyclization of α,β-unsaturated ketones was more likely to occur at the β-position because of the larger FMO coefficient. This was confirmed when $C_{10}H_8Na$ caused reductive cyclization of 4,5-secocholest-5-en-3-yn-7-one (**7**) whereas the isomeric 6-en-5-one (**8**) failed to cyclize. The product was unambiguously characterized as 3-methylene-*A*-nor-5β-cholestan-7-one (**20**).

For several years we have been engaged in an in-depth study of reductive cyclization using alkali metals directly or through the derived aromatic radical ions.[1-3] Whereas cyclization of **1a** under the Stork conditions[4] gave the "overreduction" product 3-methyl-*A*-norcholest-3(5)-ene, use of *t*-BuOH gave a mixture of this and **2a** while naphthalene sodium yielded the latter exclusively. The mechanism given in Scheme I was established for the reaction of **1b** with naphthalene sodium in THF.

The stereoselective formation of A:B cis steroids and the initial syn[5] addition across the acetylene noted in the

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