is gratefully acknowledged. We would also like to thank Dr. Roger Crecely of the University of Delaware for obtaining and discussing the ^{1}H and ^{13}C NMR spectra, reported in this work, with us. Purchase of the Bruker WM 250 was supported, in part, by a grant (GM 27616) from the National Institutes of Health.

Registry No. **2a**, 89726-11-4; **2b**, 89726-13-6; **2c**, 92816-79-0; **2d**, 89726-36-3; **2e**, 89726-27-2; **2f**, 89726-29-4; **2g**, 89726-26-1; **2h**, 89726-28-3; **2i**, 89726-25-0; **6a**, 92816-80-3; **6b**, 92816-81-4; **6c**, 92816-82-5; **6d**, 92816-83-6; **9e**, 92816-84-7; **9f**, 92816-85-8; **9g**, 92816-86-9; **9h**, 92816-87-0; **9i**, 92816-88-1; **10f**, 92816-94-9; **10g**, 92816-95-0; **10h**, 92816-96-1; **13e**, 92816-92-7; **13f**, 92816-93-8; **13i**, 92816-91-6; **14g**, 92816-89-2; **14h**, 92816-90-5; $LiAlH_4$, 16853-85-3.

Supplementary Material Available: Full IR, ^{1}H and ^{13}C NMR, and mass spectral data for compounds **6** and **9** (6 pages). Ordering information is given on any current masthead page.

Heterogeneous Catalysis in Organic Chemistry. 3. Competitive Adsorption of Solvents during Alkene Hydrogenations[1]

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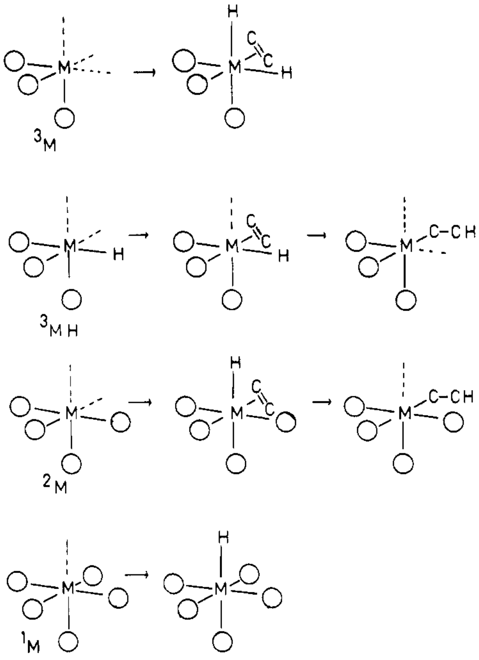
A single turnover reaction sequence has been used to determine the extent to which solvent can compete for adsorption sites in the hydrogenation of alkenes over Pt and Pd catalysts. Both methanol and ethanol are adsorbed readily on both Pt and active Pd catalysts converting the ^{3}M alkene saturation sites into ^{2}M isomerization sites and original ^{2}M sites into unreactive ^{1}M sites. *tert*-Butyl alcohol interacts only slightly with Pt catalysts presumably because of steric factors, but such restraints are not exhibited with Pd species. Over Pd the *tert*-butyl alcohol has adsorption characteristics similar to ethanol. 2-Propanol, on the other hand, enters into the reaction as a hydrogen donor in a transfer hydrogenation. THF and acetic acid are also adsorbed on the metal surface, but with THF there is little if any increase in isomerization, only a decrease in saturation capability. Acetic acid lies somewhere between THF and methanol. Other solvents such as ethyl acetate, ether, and acetone have little, if any, effect on catalyst activity.

Solvents are an important part of many heterogeneously catalyzed hydrogenations and, as such, their effect on the outcome of such reactions has been much discussed.[2–6] The solvent used in these reactions can effect their rate as well as influence the nature of the products obtained. The role of the solvent can be quite varied.[2] It can serve as a diluent to lessen the probability of interaction between molecules of reactive intermediates; it can serve as a reactant to trap intermediates and thereby prevent their further hydrogenation; it can prevent the product from precipitating onto the catalyst and deactivating it; or it can provide a medium in which a specific reaction and/or product stereochemistry is favored. In many of these cases the observed effects are due to the solvating ability of the solvent or its reactivity, dielectric constant, or acidity. Such cases are generally understood and the specific properties responsible are usually easily determined.

One aspect of the solvent effect in heterogeneously catalyzed reactions which has not been readily determinable is the nature of the solvent/catalyst interaction and the effect which this has on the outcome of the reaction.[5,6] In a study of the effect of the solvent on palladium-promoted alkene hydrogenation and isomerization, it was found that in an ethanol solvent the amount of double-bond isomerization observed was greater than that found by using a pentane solvent. To explain these results it was suggested that the ethanol was competing with hydrogen for adsorption on the active sites of the catalyst which decreased the amount of hydrogen present on the catalyst surface. This would diminish the extent of alkene saturation and increase the likelihood of isomerization.[6]

Scheme I



While this rational appeared reasonable and fit in with the classical Horiuti–Polanyi mechanism for olefin hydrogenation,[7] at that time there was no readily available means of directly determining its validity. However, the

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[1] For Part 2 of this series, see: Augustine, R. L.; Yaghmaie, F.; VanPeppen, J. F. *J. Org. Chem.* **1984**, *49*, 1865.

[2] Rylander, P. N. In "Catalysis in Organic Synthesis"; Jones, W. H., Ed.; Academic Press: New York, 1980; p 155.

[3] Baltzly, R. *J. Org. Chem.* **1976**, *41*, 920.

[4] Cerveny, L.; Vostry, B.; Ruzicka, V. *Collect. Czech. Chem. Commun.* **1981**, *46*, 2676 and previous papers by these authors.

[5] Koopman, P. G. J.; Buurmans, H. M. A.; Kieboom, A. P. G.; van Bekkum, H. *Recl. Trav. Chim. Pays-Bas* **1981**, *100*, 156.

[6] Augustine, R. L.; Nocito, V.; VanPeppen, J.; Warner, R.; Yaghmaie, F. In "Catalysis in Organic Synthesis"; Jones, W. H., Ed.; Academic Press: New York, 1980; p 173.

[7] Horiuti, I.; Polanyi, M. *Trans. Faraday Soc.* **1934**, *30*, 1164.

Table I. Product Composition Obtained with Solvent-Modified Pt/CPG Catalysts[a]

alcohol	catalyst	*n*-butane, %	cis isomer, %	trans isomer, %	metal alkyl catalyst,[b] %	1-butene, %
none	Pt-C	52	2	2	26	18
	Pt-E	41	6	5	20	27
methanol	Pt-C	20	21	19	15	25
	Pt-E	17	23	20	10	30
ethanol	Pt-C	22	19	17	17	25
2-propanol	Pt-C	56			27	17
tert-butyl alcohol	Pt-C	45			29	26
pentane	Pt-E	39	6	4	17	33
water	Pt-E	37	8	6	19	30
ethyl acetate	Pt-E	38	4	3	19	35
diethyl ether	Pt-E	28	7	6	15	44
acetone	Pt-E	29	7	5	15	43
THF	Pt-E	20	9	9	12	50
acetic acid	Pt-E	19	12	10	14	44

[a] ±1%. [b] Converted to butane by second H_2 pulse.

Table II. Product Composition Obtained with Solvent-Modified Pd/CPG Catalysts[a]

alcohol	catalyst	*n*-butane, %	cis isomer, %	trans isomer, %	metal alkyl catalyst,[b] %	1-butene, %
none	Pd-B	54	15	30		
	Pd-C	22	18	45	12	4
methanol	Pd-B	6	21	62	7	4
	Pd-C	16	17	53	12	1
ethanol	Pd-B		24	56	6	14
2-propanol	Pd-B	33	15	32	17	3
tert-butyl alcohol	Pd-B	3	31	36	4	26
pentane	Pd-C	22	17	45	12	4
water	Pd-C	21	17	48	11	3
ethyl acetate	Pd-C	18	18	52	10	2
diethyl ether	Pd-C	20	18	48	9	5
acetone	Pd-C	17	20	51	10	3
THF	Pd-C	19	21	45	9	6
acetic acid	Pd-C	9	21	58	9	3

[a] ±1%. [b] Converted to butane by second H_2 pulse.

recently developed single turnover procedure for investigating catalytic reactions[8] appears to be well suited to the study of competitive adsorption in these hydrogenation reactions. The following is a description of what was observed when this procedure was used to study single turnover alkene hydrogenations on platinum and palladium catalysts which had been exposed to alcohol vapors prior to the running of the reactions.

Results and Discussion

The single turnover procedure involves the running of stoichiometric reactions on the catalyst. When this reaction is the hydrogenation of 1-butene it is possible by an analysis of the products formed to determine the presence of different types of sites on a dispersed metal catalyst as well as the relative amounts of each of these sites present.[9] The nature of these sites is shown in Scheme I.[10] The ^{3}M (corner or kink) sites are analogous to $(Ph_3P)_2RhCl$ in the saturation of double bonds. These sites adsorb two hydrogens and a double bond to give the alkane directly.[9,10] Double-bond isomerization can take place on either ^{3}MH sites,[10] which are analogous to $(Ph_3P)_2Rh(CO)H$, or on ^{2}M (edge or step) sites which can adsorb only one hydrogen and a double bond.[9] On reaction this gives a half-hydrogenated state 1, or metal alkyl, which can then return a hydrogen to the metal to regenerate the double bond as either the starting material or an isomer, or it can await the arrival of another hydrogen with which to react to give the alkane. ^{1}M (face or terrace) sites can adsorb either a hydrogen or a double bond but not both simultaneously. These sites are not involved in the alkene hydrogenation process.[9,10]

In the standard single turnover alkene hydrogenation[8] a sample of the catalyst is first saturated with a pulse of hydrogen and the excess hydrogen is removed from the reactor in the carrier gas stream. A pulse of 1-butene of sufficient size to react with all of the adsorbed hydrogen is then passed over the catalyst and the products formed are analyzed by an on-stream gas chromatograph. The amount of butane produced is a measure of the amount of ^{3}M sites present. The extent of double-bond isomerization determines the ^{3}MH and or ^{2}M site density. Since distinguishing between these two types is not possible at present we have elected to describe all isomerization sites as ^2M_C.[9] Some alkene remains on the catalyst apparently as the half-hydrogenated state. This is removed by a second pulse of hydrogen, and the amount of butane thus formed is a measure of the number of what is referred to as ^2M_S sites.[9]

The catalysts used in this work were the 4.3% Pt/CPG (controlled pore glass) and 1.8% Pd/CPG catalysts previously described as Pt-C[9] and Pd-B[8] as well as a 4.9% Pt/CPG labelled Pt-E and another batch of 1.8% Pd/CPG called Pd-C. The product compositions observed for standard single turnover 1-butene hydrogenations run over these catalysts are listed in Tables I and II. In order to determine the effect of various solvents on these product distributions it was necessary to provide a means by which the catalysts could be saturated with the solvent vapor before the single turnover sequence was initiated. This was accomplished by modifying the apparatus in which these reactions are run[8] so the reactor tube was fitted into

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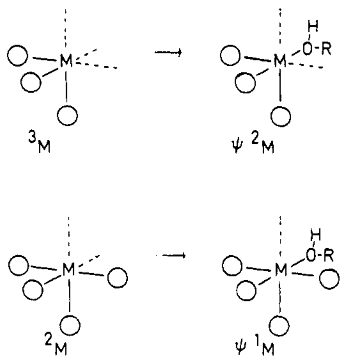
(8) Augustine, R. L.; Warner, R. W. *J. Org. Chem.* **1981**, *46*, 2614.
(9) Augustine, R. L.; Warner, R. W. *J. Catal.* **1983**, *80*, 358.
(10) Siegel, S.; Outlaw, J., Jr.; Garti, J. *J. Catal.* **1978**, *52*, 102.

Scheme II



a Tee-connector containing a septum which was placed upstream to the catalyst to allow the various solvents to be injected into the carrier gas stream flowing over the catalyst. In this way samples of the Pt and Pd catalysts were treated with various solvents and then used in the single turnover 1-butene hydrogenation. The product compositions observed in each of these hydrogenations are listed in Tables I and II.

As these data show, methanol exhibits a substantial effect on the reaction characteristics of both platinum catalysts. With these catalysts there is a marked decrease in the amount of butane formed, but this is compensated by an almost equal increase in the amount of isomerization observed. There is also a decrease in the amount of half-hydrogenated olefin remaining on the catalyst, a decrease which is offset by the amount of unreacted 1-butene observed. Essentially the same effects are observed with an ethanol-treated platinum catalyst. These results show that the methanol and ethanol are, indeed, modifying the reactive sites on the platinum surface. Specifically, it appears that the ^{3}M hydrogenation sites are being converted to ^{2}M isomerization sites and ^{2}M sites on which metalalkyl formation is favored (^{2}M$_S$) are converted to unreactive ^{1}M sites.

While an alcohol cannot be expected to completely change the catalyst morphology by adsorption on the metal surface, such adsorption can change the extent of coordinative unsaturation of the surface atoms and, as shown in Scheme II, effectively convert ^{3}M sites to ^{2}M and ^{2}M sites to ^{1}M. The fact that not all of the original sites interacted with these alcohols could be due to the presence of different kinds of ^{3}M or ^{2}M sites having either differing complexing abilities and/or different steric environments. The importance of steric parameters in heterogeneously catalyzed reactions is well established and is exemplified by a comparison of the products obtained by using a methanol-treated Pt-C catalyst and one on which *tert*-butyl alcohol was adsorbed (Table I). In the later case only a slight decrease in butane formation was observed. Apparently the *tert*-butyl alcohol was too bulky to adsorb on the more sterically restricted sites and was able to interact only slightly with the ^{3}M sites. In this case adsorption on the ^{3}M site did not result in an increase in the amount of isomeric olefins formed since the alcohol which did adsorb was too large to permit the adsorption of an olefin molecule on the same site.

As seen by the data in Table II, the effect of methanol and ethanol on the Pd-B catalyst is quite similar to that observed with platinum. There is a marked decrease in the extent of saturation indicating that these alcohols are readily adsorbed on the ^{3}M sites. There is some increase in the amount of isomerization as well as some increase in the amount of unreacted 1-butene observed, particularly with ethanol treated catalysts. In contrast to the results obtained with platinum there is also an increase over Pd-B in the extent of stable half-hydrogenated state formation. It appears, then, that some of the ^{2}M isomerization sites are being converted to ^{1}M sites and the ^{3}M sites to both isomerization, ^{2}M$_C$, and metalalkyl forming, ^{2}M$_S$, sites. With the less active Pd-C catalyst methanol promotes only a moderate decrease in butane formation, but here, too, this decrease in saturation is offset by an increase in isomerization.

A major difference between these platinum and palladium catalysts is the effect exhibited by *tert*-butyl alcohol on these species. As mentioned previously with platinum, steric factors are apparently quite important in defining the adsorption characteristics of the various types of sites. However, with palladium the product composition obtained with a *tert*-butyl alcohol treated catalyst is very similar to those found by using methanol and ethanol. Thus, either steric factors are not as important in the adsorption of alcohols on palladium or this adsorption is strong enough to overcome these steric effects.

The effect of 2-propanol on the product composition obtained with Pt-C and Pd-B is quite different from the other data listed in Tables I and II. The amount of butane formed over the 2-propanol treated catalyst was greater than that formed in the standard Pt-C catalyzed single turnover. A similar, though less pronounced, effect was also observed with 2-propanol treated Pd-B catalysts. This indicated that more hydrogen must be available in this system than that which is chemisorbed on the catalyst surface. Since secondary alcohols can serve as a hydrogen source in a transfer hydrogenation,[11] it appeared that some of the hydrogen used in the butane formation must be coming from the 2-propanol. To verify this samples of Pt-C and Pd-B were placed in reactor tubes and saturated with portions of 2-propanol. The excess alcohol was swept out of the reactors and pulses of 1-butene were then passed over the catalyst. Analysis of the products of these reactions showed that 40–60% of the 1-butene had been converted to butane. Subsequent 1-butene pulses, however, passed through the reactors unchanged.

To examine the effect which some less common hydrogenation solvents can have on platinum and palladium catalysts, portions of Pt-E and Pd-C were exposed to pentane, ethyl acetate, acetone, diethyl ether, tetrahydrofuran (THF), acetic acid, and water and then used in the single turnover reaction procedure. The results obtained are also listed in Tables I and II. With the Pt-E catalyst ethyl acetate and pentane had essentially no effect on the outcome of the single turnover reaction while ether and acetone had only a slight effect, indicating that with these solvents there is little or no adsorption on the platinum catalyst. With THF and acetic acid a more pronounced interaction with the catalyst is observed, one that is almost as strong as that found with methanol. The presence of water, though, had only a negligible effect on the single turnover results.

In contrast to what was observed with methanol, ethanol, and, to some extent, acetic acid, the decrease in butane formation that occurs in the presence of these other solvents is not accompanied by a corresponding increase in the observed amount of isomerization. These results parallel those found with *tert*-butyl alcohol as discussed above. This similarity along with the difference noted between the ether and the THF modified reactions make it likely that steric factors are also operative in these other

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[11] Nishiguchi, T.; Tagawa, T.; Imai, H.; Fukuzumi, K. *J. Am. Oil Chem. Soc.* **1977**, *54*, 144. Nishiguchi, T.; Takeshi, T.; Imai, H.; Yoshikozu, Y.; Fukuzumi, K. *J. Catal.* **1976**, *41*, 249.

solvent systems as well. Thus, the extent to which a solvent is adsorbed on the various types of sites present on a catalyst surface is determined by both electronic and steric considerations. On platinum maximum adsorption with minimum steric requirements occurs with methanol or ethanol. With THF adsorption is strong but steric factors are present which prevent the modified ^{3}M sites from interacting with the olefin and promoting isomerization. Acetic acid lies somewhere between. With the other solvents either the electronic character of the oxygen is not sufficient for strong adsorption or there are steric factors which prevent it. The lack of catalyst interaction by water was anticipated from hard/soft ligand considerations and by the report that water was not adsorbed on a Pt (111) face in a single-crystal adsorption study.[12]

Trends similar to these were also observed with Pd-C (Table II), but, as mentioned previously, the effects are much less pronounced. Water, pentane, and ether show no effect while ethyl acetate, acetone, THF, and methanol promote only a slight change in the single turnover results. A large effect is found with acetic acid. Because of the low activity of the Pd-C catalyst, though, these results are not very conclusive. Based on the general similarity observed between Pt-C and the more active Pd-B in their interaction with alcohols, it is anticipated that the steric and electronic considerations presented above for platinum would also be applicable to palladium catalysts with the exception that adsorption of the solvent on palladium appears to be less influenced by steric factors than it does on platinum.

These results show that the adsorption of solvent molecules can have an effect on the behavior of a supported metal catalyst. With both platinum and palladium, particularly the more active catalysts, this effect is most pronounced with methanol and ethanol which on adsorption apparently change the nature of the active sites present on the catalyst surface. This, in turn, can lead to a decrease in reaction rate, an enhancement of double-bond isomerization, and, possibly, a change in reaction selectivity. On the other hand, solvents such as pentane (or other alkanes) and ethyl acetate have little, if any, effect on the nature of the active sites on the metal surface, and reactions run in these solvents can be expected to proceed more rapidly and probably have fewer competitive side reactions.

Experimental Section

The catalyst preparations, the gas chromatographic conditions, and the gas purification procedure were described in previous publications.[8,9] The catalysts used were the previously described 4.3% Pt/CPG (controlled pore glass) (Pt-C)[9] and a 1.8% Pd/CPG (Pd-B).[8] Pt-E is a 4.9% Pt/CPG prepared by reduction of the CPG-supported Pt complex[8] in a stream of H_2 at 200 °C for 2.5 h. Pd-C is a 1.8% Pd/CPG prepared by the reduction of the CPG supported Pd complex[8] in hydrogen at 200 °C for 2 h. The single turnover apparatus discussed previously[8] was modified by having the reactor tubes fitted into air-tight Tee-connectors containing septa which were placed upstream of the catalyst to allow the entrained solvent vapors to pass across the catalyst. To prevent the solvents from possibly damaging the analytical GC column, a valving arrangement was used which permitted excess solvent vapor to bypass the column but still pass through the detector. In this way it could be determined when the excess solvent was eluted so the turnover procedure could be initiated.

The alcohols used were distilled from sodium and degassed before use. The water used was triply distilled, degassed by boiling, and cooled under N_2 before use. The THF was placed over KOH pellets for 48 h, distilled from CaH_2, and stored over 5-Å molecular sieves. The acetic acid was refluxed with acetic anhydride for 2 h and then distilled. The pentane was hydrogenated over 5% Pd/C for 12 h at 30 psig. The acetone was stored over anhydrous $MgSO_4$ and distilled from the mixture. The ethyl acetate was purified by distillation and the ether was commercial anhydrous. All solvents were stirred for 1 h over 5% Pt/C to remove any catalyst poisons, decanted, and degassed with N_2 immediately before use.

Procedure. A 4–5-mg sample of the catalyst was placed between plugs of Pyrex glass wool in the reactor and swept with a 30 mL/min flow of deoxygenated zero grade helium for 1 h. A 0.5–1-μL portion of the solvent was injected into the carrier gas stream and passed over the catalyst. The excess solvent was eluted through the GC column bypass. When all the excess solvent was removed from the reaction system as indicated by a return to a normal base line, a 10-μL pulse of H_2 was passed over the catalyst followed after 1 min by a 10-μL pulse of 1-butene. After ten more minutes, another 10-μL pulse of H_2 was added to react with the metalalkyl on the catalyst. The products formed from this single turnover were analyzed by an on-stream gas chromatograph. This turnover sequences, H_2–ene–H_2, was repeated 3 or 4 times for each reaction system. In most cases there was little change in the product composition from turnover to turnover. Data for duplicate runs were reproducible to within ±2%.

In the *transfer hydrogenations* 5.0-mg samples of Pt-C and Pd-B were placed in reactor tubes and 0.5 μL of *i*-prOH injected into the system. After the excess alcohol had eluted, a 10-μL pulse of 1-butene was passed over the catalyst. On GC analysis the product composition from the Pt-C catalyzed reaction was found to be 60% butane, 39% 1-butene, and traces of *cis*- and *trans*-2-butene. Similar results were found for the Pd-B catalyzed process.

Registry No. Pt, 7440-06-4; Pd, 7440-05-3; THF, 109-99-9; methanol, 67-56-1; ethanol, 64-17-5; 2-propanol, 67-63-0; *tert*-butyl alcohol, 75-65-0; acetic acid, 64-19-7; ethyl acetate, 141-78-6; diethyl ether, 60-29-7; acetone, 67-64-1; water, 7732-18-5; pentane, 109-66-0; 1-butene, 106-98-9.

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[12] Garwood, G. A., Jr.; Hubbard, A. T. *Surf. Sci.* **1982**, *118*, 223.