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Using Correlations to Compare Additions to Alkenes: Homogeneous Hydrogenation by Using Wilkinson's Catalyst

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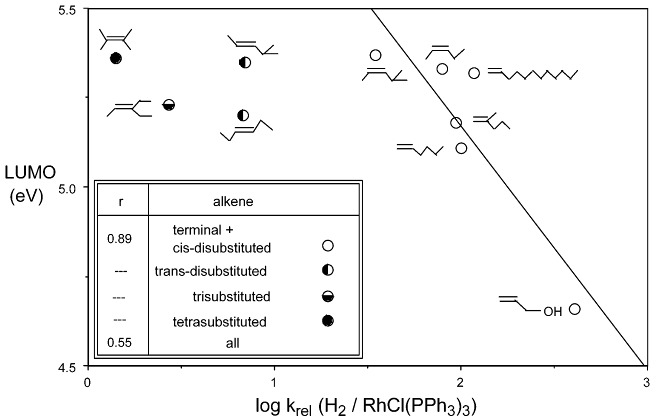

Plots of the logarithms of relative rates of homogeneous catalytic hydrogenation of alkenes (log k_{rel} values) by using Wilkinson's catalyst versus their ionization potentials (IPs) and versus their lowest unoccupied molecular orbital energy levels (LUMOs) display good-to-excellent correlations. The correlations indicate that the rate-determining step of this reaction is a nucleophilic addition to the alkene double bond, which is dependent upon both electronic effects and steric effects. This conclusion is in agreement with only two of three previously proposed mechanisms for the reaction, effectively ruling out one in which the rate-determining step involves electrophilic addition to the alkene. Characteristics of the analysis using these correlations are compared and contrasted with other additions to alkenes, such as the Wacker oxidation, to probe patterns in transition state characteristics.

Introduction

In this study, we apply to homogeneous catalytic hydrogenation by using Wilkinson's catalyst a relatively new technique that can reveal mechanistic similarities of alkene addition reactions by comparing their correlation plots. This simple method[1a–h] ascertains the relative importance of electronic and steric effects in addition reactions of alkenes by correlating logarithms of relative reaction rates (log k_{rel} values) versus the alkene ionization potentials (IPs), versus their highest occupied molecular orbital energy levels (HOMOs), and sometimes versus their lowest unoccupied molecular orbital energy levels (LUMOs). This technique provides synthetically useful information about the selectivity of a reaction toward

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* To whom correspondence should be addressed. Tel: (405) 325-2288. Fax: (405) 325-6111.

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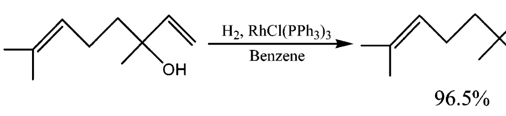
different types of alkene π bonds.[1a−h] In some cases, it has enabled mechanism selection from a group of proposed mechanisms. Examples of reactions of alkenes in which this was done are (1) classifying the mechanism of oxymercuration as being similar to hydroboration rather than bromination,[1b] (2) analyzing the three-membered cyclic intermediate (or product) mechanism in alkene bromination, arylsulfenyl chloride addition, oxidation via peracetic acid, and dichlorocarbene addition versus the four-membered cyclic intermediate mechanism in nitrosyl chloride addition,[1a,e] (3) selecting one of two proposed mechanisms for oxidation by using palladium chloride,[1g] and (4) supporting a 2 + 3 cycloaddition mechanism but disfavoring the 2 + 2 cycloaddition mechanism for alkene oxidation by chromyl chloride, by chromic acid, and by osmium tetroxide.[1h] In each study, we used the rationale that reactions with similar mechanisms give correlation plots that are similar in appearance. It is desirable to investigate similarly more reactions of mechanistic and synthetic importance, not only to gather additional information about the reactions but also to explore further the application of this analysis technique. Therefore, we report the application of this technique to the homogeneous catalytic hydrogenation of alkenes by using Wilkinson's catalyst, as a result of the interest in its mechanism[2−5] and its synthetic[6a−f] and industrial[6g,h] importance.

Background

Homogeneous catalytic hydrogenation of alkenes in the presence of Wilkinson's catalyst $RhCl(PPh_3)_3$, developed in 1965 by Wilkinson and co-workers,[7] is a widely studied[2−7] homogeneous catalytic hydrogenation method used in organic synthesis[6a−f] and reported to be industrially important.[6g,h] Using modifications of Wilkinson's catalyst, homogeneous asymmetric hydrogenation reactions, catalyzed by rhodium diphosphine chiral complexes, were developed later by Knowles[8a−c] and Noyori.[8d,e] This synthetic method enabled the production of a single predicted enantiomer, of great significance in the syntheses of pharmaceutical products.[3g,4b,c,8] One early industrial scale synthetic application was synthesis of L-DOPA, which is useful in the treatment of Parkinson's disease and which is produced by enantioselective hydrogenation of an α-amino acid catalyzed by a rhodium complex containing the chiral diphosphine ligand DiPAMP.[8c] A wide range of similar catalysts has been applied widely in industrial syntheses of drugs and other materials.[3g,4b,c,8]

The basic reaction (eq 1) shows sensitive selectivity to different alkene double bonds with different substituents on it[6a,e,f] and can be easily carried out under mild reaction conditions (room temperature and atmospheric pressure of H_2).[6a−c]



(1)

Several different reaction mechanisms[3a−f,4a,5] have been proposed for this homogeneous hydrogenation catalytic cycle, but the "hydride route" (as opposed to the "alkene route"[6a] or "substrate route"[2h]) is believed to be the predominant pathway.[6a] Three proposed hydride route mechanisms of this reaction are shown in Schemes 1−3.

There are five steps in the reaction sequence in Scheme 1:[3b−f] (1) PPh_3 ligand dissociation **1** $\rightleftarrows$ **2**; (2) hydrogen oxidative addition **2** $\rightleftarrows$ **3**; (3) alkene coordination **3** $\rightleftarrows$ **4**; (4) alkene migratory insertion into the Rh−H bond **4** → **5**; and (5) alkyl reductive elimination **5** → **2**. In this mechanism, the alkene insertion **4** → **5** is considered to be the rate-determining step,[3a−f] and the key intermediate is **4**, an octahedral dihydride alkene complex $RhH_2Cl(alkene)(PPh_3)_2$. All other steps are fast relative to the alkene insertion **4** → **5**.[2c−e,3a−f] Positions occupied by S (S = solvent) in **2**, **3**, **5** are considered to be either vacant or coordinated to a solvent molecule.[3b] Some later

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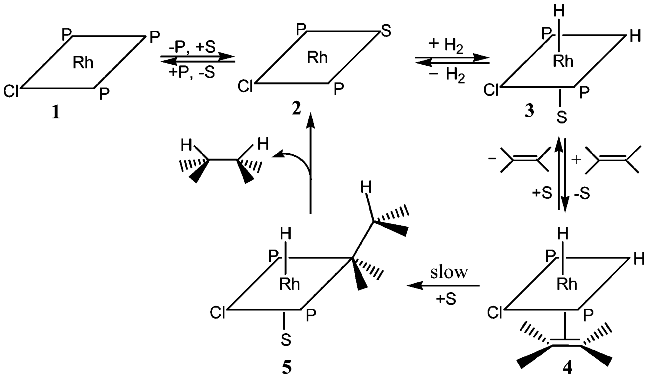
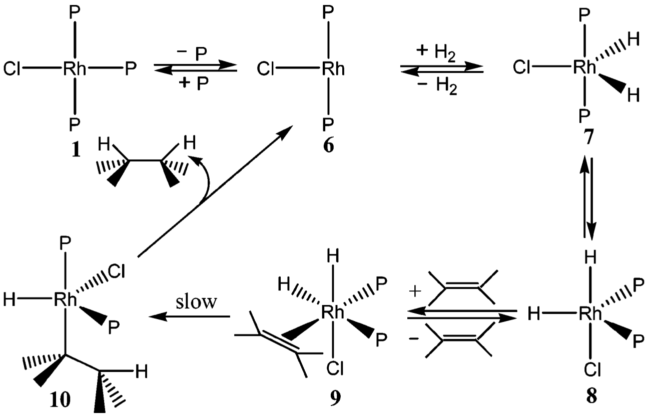
SCHEME 1. First Hydride Route Mechanism Proposed for Hydrogenation of Alkenes by Using Wilkinson's Catalyst[3b–f] (P = PPh_3 and S = Benzene as Solvent)



SCHEME 2. Second Hydride Route Mechanism with Isomerization, Proposed for Hydrogenation of Alkenes by Using Wilkinson's Catalyst[4a] (P = PPh_3).

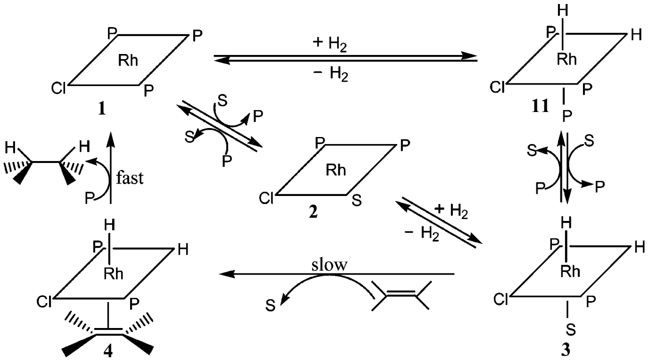


studies[6a,9a] tend to support the idea that a solvent molecule is associated with the Rh center at each of those positions.

A second hydride route mechanism[4a] differs slightly regarding (a) the structures of the key intermediates (**9** in Scheme 2 versus **4** in Scheme 1) and (b) the involvement of the solvent molecules because no solvent molecule is involved in this proposed mechanism. In this alternative, an isomerization (**7** ⇄ **8**) precedes the formation of a key intermediate **9**, which possesses *cis* biphosphine ligands. All of these first four steps (**1** ⇄ **6**, **6** ⇄ **7**, **7** ⇄ **8**, and **8** ⇄ **9**) are considered to be fast equilibria.[4a] Then, the rate-determining alkene insertion (**9** → **10**) is followed by a fast alkyl reductive elimination (**10** → **6**) to regenerate **6**.[4a,6h]

In an ab initio computational mechanistic investigation[9a,b] of the Scheme 1 pathway, the potential energy profile for the full catalytic cycle of alkene hydrogenation by Wilkinson's catalyst was studied. The geometries of the transition states as well as of the intermediates were determined at the RHF/ECP level by using a variety of basis sets, for each step of the reaction cycle. It was found that the alkene insertion step has the highest energy barrier in the full catalytic cycle of this reaction, predicting it to be the rate-determining step of this reaction. This conclusion is consistent with both mechanisms shown in Schemes 1 and 2.[3a–f,4a]

SCHEME 3. Third Hydride Route Mechanism[5] (P = PPh_3, S = Benzene as Solvent)[a]



[a] Stereochemistry was not specified and is given solely to facilitate comparison with structures in Schemes 1 and 2.

A third hydride route mechanism[5] (Scheme 3) was proposed on the basis of kinetic analyses indicating that a solvent molecule S (S = benzene) is involved in the catalytic sequence and that the rate-determining step, which is preceded by four fast complexation equilibria[5] in two different routes, is formation of the 6-coordinate intermediate **4**. Then, this 6-coordinate intermediate **4** undergoes a fast decomposition to yield the alkane product and to regenerate Wilkinson's catalyst **1**.[5]

Another totally different mechanism for alkene hydrogenation in the presence of Wilkinson's catalyst and various Lewis acids, such as $AlCl_3$, BF_3, $AlPh_3$, etc., has been proposed.[2f] However, the reaction conditions used in that study[2f] are so different from those discussed above[3a–f,4b,5] that this may constitute a different reaction, and a mechanistic comparison is probably invalid.

Results and Discussion

A. Correlation Patterns Probe Addition Reaction Mechanisms. Information about electronic and steric effects is revealed from the plots of log k_{rel} values versus IPs. The IP is an appropriate comparator because it is a measure of the amount of energy required to remove an electron from the π bond and because it is independent of steric effects. Most of our previously studied reactions gave good-to-excellent correlations with positive slopes;[1a–c,e,f,h] some of the resulting plots each had a single line of correlation,[1a,b,e,f,h] and some each had nearly-parallel lines of correlation.[1a–c,f]

In this way, these correlation plots gave information about steric effects in the reactions. Reactions of alkenes (such as bromination,[1b,f] epoxidation,[1a] carbene addition,[1e] oxidation by chromyl chloride and by chromic acid,[1h] etc.) that lack significant steric effects display in their plots of log k_{rel} values versus IPs a single correlation line consisting of all alkenes, regardless of degree of substitu-

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(9) (a) Daniel, C.; Koga, N.; Han, J.; Fu, X. Y.; Morokuma, K. *J. Am. Chem. Soc.* **1988**, *110*, 3773−3787. (b) Koga, N.; Daniel, C.; Han, J.; Fu, X. Y.; Morokuma, K. *J. Am. Chem. Soc.* **1987**, *109*, 3455−3456. (c) Hornback, J. M. *Organic Chemistry*; Brooks/Cole: New York, 1998; p 259. (d) Connors, K. A. *Chemical Kinetics*; VCH: New York, 1990; p 223.

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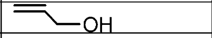
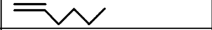
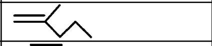
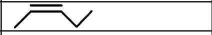
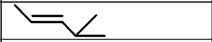
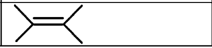
TABLE 1. IPs(eV), LUMOs(eV), and Relative Rates of Catalytic Hydrogenation of Alkenes by Using Wilkinson's Catalyst, $RhCl(PPh_3)_3$

No.	alkene	IP[a]	LUMO	k_{rel}[b]
1		10.16[c]	4.66	410[d]
2		9.59[e]	5.32	117.9
3		9.48	5.11	100
4		9.08	5.18	93.1
5		9.04	5.33	79.3
6		8.98	5.37	34.5
7		8.97	5.35	6.9
8		8.97	5.20	6.8[d]
9		8.57[f]	5.23	2.7[d]
10		8.27	5.36	1.4[d]

[a] Reference 13a, unless otherwise noted. [b] References 7d, 12a. [c] Reference 13b. [d] Reference 7d; converted to relative rates from rates of H_2 consumption. [e] Reference 13c. [f] Reference 13d.

tion. Reactions of alkenes with significant steric effects (such as hydroboration,[1b] oxymercuration,[1b] silver ion complexation,[1a] diimide addition,[1c] etc.) give plots with multiple lines of correlation.

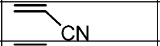
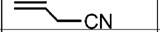
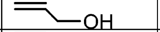
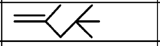
However, for the reaction of alkenes with $PdCl_2/H_2O$,[1g] we found multiple lines with negative slopes in the plots of alkene IP versus log k_{rel} value. The lines indicated a good-to-excellent correlation. Initially, in this nucleophilic addition, we planned to explore a correlation between log k_{rel} values and alkene electron affinities (EAs), but EAs are not readily available for a large selection of alkenes. However, calculated alkene LUMOs are good estimates for experimental EA values[10,11] if a suitable computational method is selected. Therefore, using a selection of computational methods, we examined the correlation of calculated alkene LUMOs versus experimental alkene EAs and used the method (6-31G*) that gave the best agreement.[1i]

Previous studies indicated that reactions with similar rate-determining transition-state structures yield correlation plots that have similar slopes and numbers of lines. Reactions that have different rate-determining transition-state structures usually yield different types of correlation plots, but this is not necessarily the case. As clarification, if different types of plots are obtained, then rate-determining transition states in the reactions concerned must have significant differences; however, similar correlation plots do not necessarily indicate similar rate-determining transition-state structures.

B. Correlation in Hydrogenation of Alkenes by Using Wilkinson's Catalyst. Relative reaction rates[7d,12a,b] for homogeneous hydrogenation of alkenes in the presence of Wilkinson's catalyst, alkene IPs,[13a−h] and alkene LUMOs are given in Tables 1 and 2. As was done previously,[1] cyclic alkenes and aryl alkenes are excluded here in order to avoid complications due to ring strain or conjugation with phenyl.

The plots in Figures 1−4 show good-to-excellent[14] correlations of log k_{rel} values versus alkene IPs and versus alkene LUMOs for the terminal alkenes and *cis*-disubstituted alkenes. However, the data points for alkenes with different steric requirements, such as *trans*-disubstituted, trisubstituted, and tetrasubstituted alkenes, are deviant from the correlation lines, which indicates that the rate-determining step of homogeneous

TABLE 2. IPs(eV), LUMOs(eV), and Relative Rates of Catalytic Hydrogenation of Alkenes by Using Wilkinson's Catalyst, $RhCl(PPh_3)_3$

No.	alkene	IP[a]	LUMO	k_{rel}[b]
11		10.91[c]	2.80	1470
12		10.72[c]	3.15	350
13		10.18[d]	4.22	490
14		10.16[e]	4.66	340
15		9.85[c]	4.47	160
16		9.48	5.11	100
17		9.15[f]	5.51	180
18		9.08	5.18	69
19		8.91	5.00	41
20		8.84	5.32	54
21		8.83	5.31	17

[a] Reference 13a, unless otherwise noted. [b] Reference 12b. [c] Reference 13f. [d] Reference 13g. [e] Reference 13b. [f] Reference 13h.

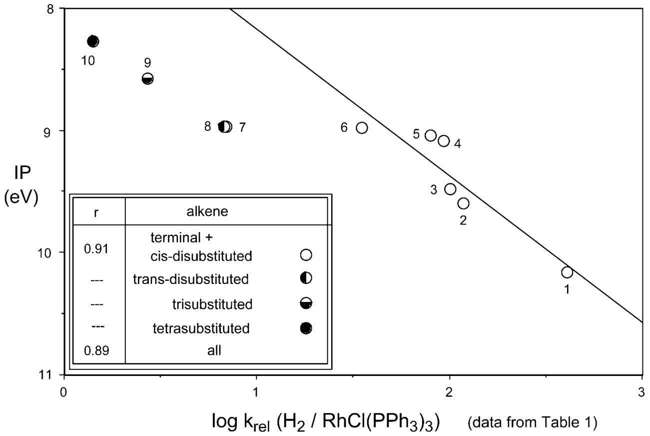


FIGURE 1. Plot of the log k_{rel} values for homogeneous hydrogenation of alkenes by using Wilkinson's catalyst versus corresponding alkene IPs. Data used for this plot are given in Table 1. Correlation coefficients (*r* values) are given in the legend for terminal alkenes + *cis*-disubstituted alkenes and for all alkenes regardless of the degree of substitution about the double bond. The correlation line in this plot refers to terminal alkenes and *cis*-disubstituted alkenes only. The *y*-axis IP data are plotted in inverse order to facilitate comparison with previous works.

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(12) (a) James, B. R. *Homogeneous Hydrogenation*; John Wiley & Sons: New York, 1973; pp 198−287. Allyl cyanide is not included in the plot because its data point falls far from the correlation line, probably as a result of the interaction of the cyanide group and the Rh metal center of the catalyst. (b) Candlin, J. P.; Oldham, A. R. *Discuss. Faraday Soc.* **1968**, *46*, 60−71.

(13) (a) Masclet, P.; Grosjean, D.; Mouvier, G.; Dubois, J. *J. Electron Spectrosc. Relat. Phenom.* **1973**, *2*, 225−237. (b) Katrib, A.; Rabalais, J. W. *J. Phys. Chem.* **1973**, *77*, 2358−2363. (c) Calculated by applying to the IP for 1-decene, a correction factor calculated as the difference between the IPs of 1-decene and 1-octene: 9.51 + (9.51 − 9.43) = 9.59 eV; ref 13e. (d) Calculated by applying to the IP for 3-ethyl-3-hexene, a correction factor calculated as the difference between the IPs of *cis*-2-pentene and *cis*-3-hexene: 8.48 + (9.04 − 8.95) = 8.57 eV; ref 13a. (e) Hiraoka K. *J. Phys. Chem.* **1981**, *85*, 4008−4015. (f) Houk, K. N.; Munchausen, L. L. *J. Am. Chem. Soc.* **1976**, *98*, 937−946. (g) Willett, G. D.; Baer, T. *J. Am. Chem. Soc.* **1980**, *102*, 6774−6779. (h) Friege, H.; Klessinger, M. *J. Chem. Res., Synop.* **1977**, 208−209.

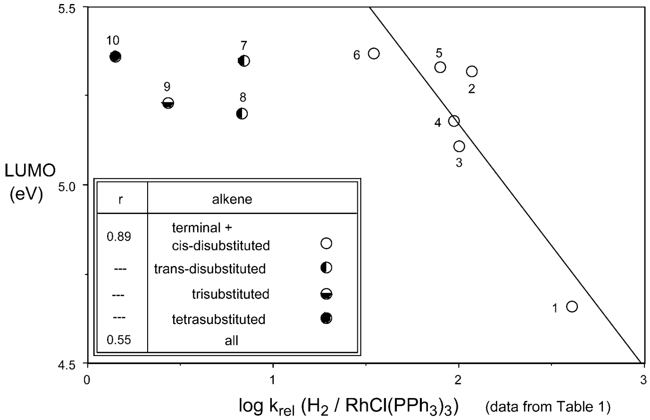

FIGURE 2. Plot of the log k_{rel} values for homogeneous hydrogenation of alkenes by using Wilkinson's catalyst versus corresponding alkene LUMOs. Data used for this plot are given in Table 1. The correlation line in this plot refers to terminal alkenes and *cis*-disubstituted alkenes only.

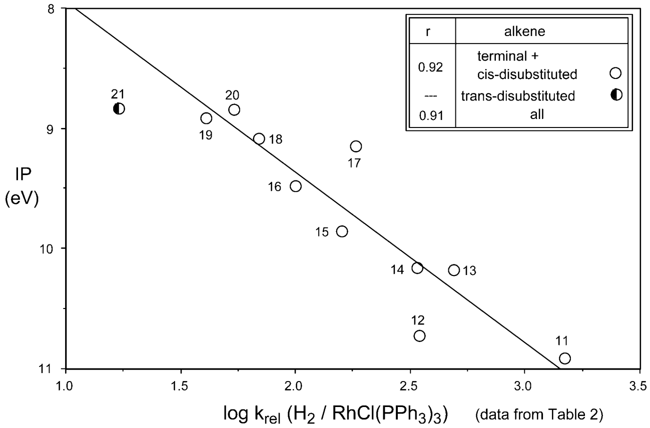

FIGURE 3. Plot of the log k_{rel} values for homogeneous hydrogenation of alkenes by using Wilkinson's catalyst versus corresponding alkene IPs. Data used for this plot are given in Table 2. The correlation line in the above plot refers to terminal alkenes and *cis*-disubstituted alkenes only.

hydrogenation of alkenes in the presence of Wilkinson's catalyst is dependent upon both steric effects and electronic effects. The correlation line in each plot of Figures 1−4 is for terminal alkenes and *cis*-disubstituted alkenes that have similar steric requirements in this reaction, but not for all alkenes regardless of the degree of substitution of the alkene double bonds. Although in some plots it seems that the plot with all alkenes gives just as good results as the plot with terminal + *cis*-disubstituted alkenes, this is not the case for all figures. However, the plot with terminal alkenes + *cis*-disubstituted alkenes gives at least "good"[14] correlation in each case.

C. Nucleophilic versus Electrophilic Characteristics. The negative slopes of the plots in Figures 1−4 agree with previous findings[15a−d] that the rate-determining step in this reaction is a nucleophilic process, with a higher IP or lower LUMO corresponding to a higher relative reaction rate. The slopes in the plots are opposite to those in most of our previous investigations[1a−h] which explored electrophilic additions. However, the correlation in this reaction is similar to that of $PdCl_2$ oxidation (multiple lines with negative slopes),[1g] which is also a nucleophilic addition reaction.

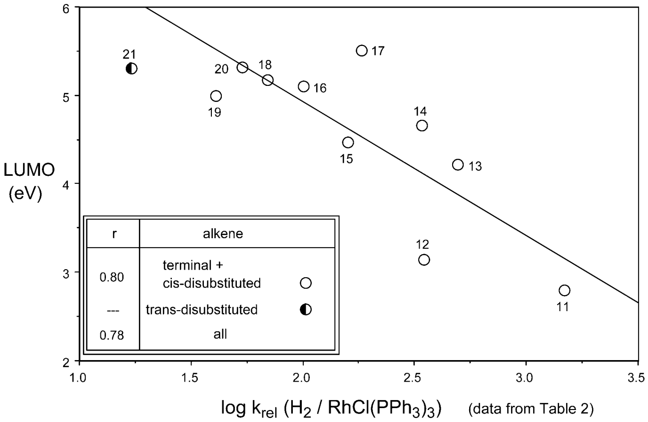

FIGURE 4. Plot of the log k_{rel} values for homogeneous hydrogenation of alkenes by using Wilkinson's catalyst versus corresponding alkene LUMOs. Data used for this plot are given in Table 2. The correlation line in the above plot refers to terminal alkenes and *cis*-disubstituted alkenes only.

The conclusion that the rate-determining step in homogeneous catalytic hydrogenation involves nucleophilic attack on the alkene is consistent with both the first and the second proposed mechanisms (Schemes 1 and 2).[3b−f,4a] These mechanisms have virtually identical rate-determining steps, each proposed to be an intramolecular alkene insertion (**4** → **5** in Scheme 1 and **9** → **10** in Scheme 2). The structural changes during the insertion have been described[6a] as a symmetrical alkene η^2-coordination, shifting to a η^1-coordinated species, and picking up the hydride from the metal at its uncoordinated carbon. The proposed rate-determining step is a nucleophilic addition,[6b,d] which our results support.

However, the above conclusion disfavors the third proposed mechanism (Scheme 3),[5] in which alkene complexation (**3** → **4** in Scheme 3) is predicted to be the rate-determining step. In this step, the alkene displaces benzene and coordinates to the Rh center, which constitutes an electrophilic attack of Rh on the alkene; our results, which indicate a rate-determining nucleophilic attack on the alkene, are at odds with this proposed mechanism.

D. Comparison with Other Similar Addition Reactions. The catalytic hydrogenation of alkenes by using Wilkinson's catalyst has similarities to and differences from the $PdCl_2$ oxidation of alkenes (the Wacker reaction): (1) the slopes of the lines in the log k_{rel} versus IP and log k_{rel} versus LUMO plots of both reactions are negative, which indicates that both reactions are nucleophilic addition reactions; (2) the rate-determining steps in Scheme 1[3b,c] and Scheme 2[4a] are both alkene insertion processes similar to that for $PdCl_2$ oxidation;[16a−c] (3) the rate-determining steps in catalytic hydrogenation in the presence of Wilkinson's catalyst (eq 2) and in the Wacker

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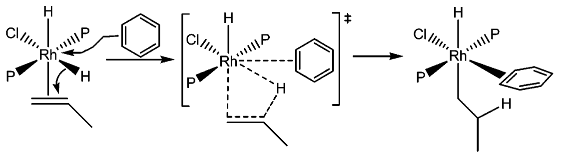
[14] Rowntree, D. *Statistics Without Tears*; Scribner: New York, 1981; p 170.

[15] (a) Burger, B. J.; Santarsiero, B. D.; Trimmer, M. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 3134−3146. (b) Doherty, N. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 2670−2682. (c) Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 6148−6149. (d) Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4308−4320.

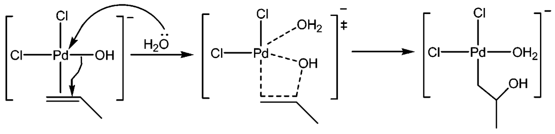
[16] (a) Henry, P. M. *J. Am. Chem. Soc.* **1966**, *88*, 1595−1597. (b) Henry, P. M. *Adv. Chem. Ser.* **1968**, *70*, 127−154. (c) Wan, W. K.; Zaw, K.; Henry, P. M. *Organometallics* **1988**, *7*, 1677−1683.

oxidation (eq 3) have been proposed to involve similar four-center transition states; (4) data points in plots for $PdCl_2$ oxidation[1g] separate naturally into different sterically similar alkene groups, as do those in the plot for alkene hydrogenation, although some differences still exist between them; and (5) geminal and vicinal cis disubstituted alkenes fall into the same sterically similar group as the monosubstituted alkenes in hydrogenation (Figures 1−4), whereas all disubstituted alkenes fall into a different group in $PdCl_2$ oxidation,[1g] which implies greater steric effects in the latter for reasons that cannot be specified.



(2)

I_d mechanism (P = PPh_3)



(3)

I_a mechanism

The display of similar electronic effects in the two reactions is not surprising. Rh and Pd might be expected to form organic derivatives that have similar such characteristics, based on their joint membership in the second triad of groups 9 and 10; they are both "platinum metals".[17] Similar nucleophilic characteristics in both reactions could be rationalized by the nucleophilic attacks upon one carbon atom of the alkene double bonds by hydride in the hydrogenation and by hydroxide in the Wacker reaction.

The different steric effects in the two reactions could be derived from steric congestion at an alkene carbon, from steric congestion about the central metal, or from other sources. Several explanations for the differing steric effects in the transition states of the two reactions can be offered:

(A) The different sizes of the groups migrating to the alkene carbon must be considered; OH is larger than H, so its migration might be expected to cause greater steric congestion at the alkene carbon in that reaction, as observed.

(B) The different sizes of the solvent molecules entering as ligands are significant. An entering benzene ligand might be expected to cause more congestion than an entering H_2O ligand (eqs 2 and 3). However, this is inconsistent with lower steric effects in the Wilkinson reduction than in the Wacker Reaction, so the entering solvent does not produce the observed steric effect in these reactions. This supports the practice of omitting solvent from mechanistic schemes drawn for this reaction, often done by Halpern[3] and by Brown.[4]

(C) The smaller steric effect despite a larger entering solvent ligand in alkene hydrogenation (eq 2) than in the Wacker reaction (eq 3), might also be explained by the former being an I_d (dissociative interchange[18]) process of an octahedral complex and the latter being an I_a (associative interchange[18]) process of a square planar complex. The designations "I_d process" and "I_a process" follow the generalized nomenclature for mechanisms of ligand exchange;[18] an I_d process has both the entering and leaving ligands more dissociated and farther apart than in an I_a process as depicted in eqs 2 and 3. Although we have no experimental measurements to compare distances between the metals and entering ligands in the transition-state structures, there are some data available for similar ground-state molecules. Studies show that the average distance between Rh and the two coordinated benzene carbons in the product $[Rh(\eta\text{-}C_5H_5)\{\beta,\alpha,1,2\text{-}\eta\text{-}C_6H_5C(Ph){=}CH_2]$ is about 2.21 Å,[19a] which is greater than the distance (2.10 Å) between Pd and O in the product $[Pd(C_2H_4OH)(H_2O)Cl_2]$.[19b,c]

(D) However, the calculated bond lengths of Pd−Cl and Pd−C are 2.30 and 2.20 Å,[19b] respectively, in the four-membered transition state of the rate-determining insertion of $[PdCl_2H(C_2H_4)]^-$, and the calculated bond lengths of Rh−Cl and Rh−C are 2.30 and 2.21 Å,[9a] respectively, in the four-membered transition state of the rate-determining insertion of $[RhCl(PH_3)_2(C_2H_4)H_2]$. These are almost identical and, therefore, would lead one to predict similar steric effects in the transition-state structures in these two reactions.

(E) A theoretical calculation[19d] predicts the Rh−C bond strength in $Rh{-}C_2H_5$ of 50.3 kcal/mol, which is higher than that of Pd−C in $Pd{-}C_2H_5$ (40.9 kcal/mol). The stronger developing Rh−C bond in the transition state structure might cause the alkene migratory insertion transition state in catalytic hydrogenation to be later with somewhat less steric effects than in the Wacker oxidation.

(F) Calculations[9a] have predicted a late transition state for the hydrogenation of alkenes catalyzed by Wilkinson's catalyst, which is consistent with the prediction that the rate-determining step of this reaction is an endergonic process.[9c,d] A late transition state, in which only one carbon is significantly bonded to Rh and the Rh−H bond is nearly broken, could explain the reduced steric effects. In this case, electronic effects would also not be significant, because little distortable π electron density would remain in the transition state structure. This would agree with the correlation plot, i.e., closely spaced multiple lines with small slopes. Thus, a later transition state in alkene hydrogenation by using Wilkinson's catalyst than in the Wacker oxidation might also contribute to slightly smaller steric effects in the former.

It should be added that rates of catalytic reactions may not represent only the barrier of the rate-determining step, as has been assumed in the above discussion; they can be a more complex mixture, driven by the distribution of catalyst among active and inactive species. However, in this case, excellent correlations are obtained, suggesting that here a factor other than catalyst distribution prevails.

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(17) (a) Cotton, A. F.; Wilkinson, G. *Advanced Inorganic Chemistry*; John Wiley & Sons: New York, 1972; pp 990−995. (b) Heslop, R. B.; Jones, K. *Inorganic Chemistry*; Elsevier Scientific Publishing Company: New York, 1976; pp 701−703.

(18) Wilkins, R. G. *Kinetics and Mechanism of Reactions of Transition Metal Complexes*; VCH: New York, 1991; 201.

(19) (a) Wadepohl, H.; Metz, A.; Pritzkow, H. *Chem. Eur. J.* **2002**, *8*, 1591−1602. (b) Fujimoto, H.; Yamasaki, T. *J. Am. Chem. Soc.* **1986**, *108*, 578−581. (c) Bäckvall, J. E.; Björkman, E. E.; Pettersson, L.; Siegbahn, P. *J. Am. Chem. Soc.* **1984**, *106*, 4369−4373. (d) Siegbahn, P. E. M. *J. Phys. Chem.* **1995**, *99*, 12723−12729.

Conclusion

Negative slopes of correlation lines in the plots of log k_{rel} values versus IPs and versus LUMOs are obtained for hydrogenation of alkenes by using Wilkinson's catalyst. This supports previous findings that the rate-determining step of this reaction is a nucleophilic alkene addition. The multiple lines in each plot indicate that the reaction is dependent upon both electronic effects and steric effects in its rate-determining step. The method of analysis employed in this study demonstrates a simple way to predict relative reactivities of functionalized alkenes based on electronic and steric characteristics of the alkene substituents; this information will be useful in designing syntheses requiring selective reaction of one alkene functionality in the presence of another.

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