

Heterogeneous Reductions of (Diolefin)dialkylplatinum(II) Complexes on Platinum Black in Ethyl Alcohol: Kinetics, Isotopic Interchange of Hydrogen between Coadsorbed Surface Alkyls, and Comparison of Surface Alkyls Generated from the Platinum Complexes and from Olefins¹

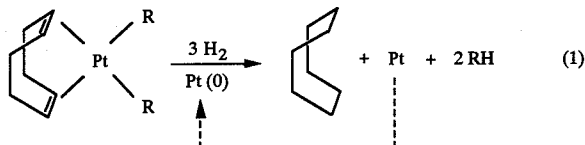
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Abstract: This paper reports an investigation of the heterogeneous hydrogenations of (diolefin)dialkylplatinum(II) complexes ((DO)PtR₂) catalyzed by platinum black in ethyl alcohol. The organic ligands of (DO)PtR₂ complexes are converted to alkanes via intermediate surface alkyls, and the platinum(II) is incorporated into the surface of the catalyst as platinum(0). These reductions exhibit two kinetic regimes: in the first, the rate of reaction is limited by the mass transport of hydrogen to the surface of the catalyst (the mass-transport-limited regime, MTL); in the second, the rate is limited by a reaction on the surface of the catalyst (the reaction-rate-limited regime, RRL). In reductions of (DO)PtR₂ complexes in *n*-hexane, interchange of H/D occurs between the surface alkyls derived from the diolefin and those derived from the R groups; in reductions in ethyl alcohol (EtOH), this interchange is eliminated by rapid exchange between D* and EtOH. Under RRL conditions, the distributions of ethanes-*d*_n produced from the reductions of (1,5-cyclooctadiene)diethylplatinum(II) ((COD)PtEt₂) and of ethylene suggest that the R* moieties generated from olefins and from platinum complexes have similar relative rates of isotopic exchange (and thus of C-H bond activation) and reductive elimination as alkane. Comparison of the distributions of propanes-*d*_n produced from the reductions under RRL conditions of (1,5-cyclooctadiene)di-*n*-propylplatinum(II), of (1,5-cyclooctadiene)diisopropylplatinum(II), and of propylene leads to the same conclusion. Under MTL conditions, the Et* moieties derived from (COD)PtEt₂ have a slower rate of C-H bond activation (relative to the rate of reductive elimination) than those derived from ethylene. Reductive elimination of the R* moieties seems to be more rapid than that of the cyclooctyl* moieties in these reactions.

Introduction

The heterogeneous, platinum-catalyzed reduction of (1,5-cyclooctadiene)dialkylplatinum(II) complexes ((COD)PtR₂) by dihydrogen on platinum black produces cyclooctane, 2 equiv of alkane, and platinum(0) (which is incorporated into the surface of the catalyst) (eq 1).²⁻⁴ This reaction proceeds by initial



adsorption of the platinum atom of the complex onto the surface of the catalyst, and generates surface alkyls from the alkyl and

diolefin moieties originally present in the organometallic complex. The surface alkyls (R*) react with surface hydrides (H*) and generate alkanes. When appropriate temperatures and pressures of dihydrogen are chosen, the rate-determining step can be chosen as the mass transport of dihydrogen to the surface of the catalyst (the mass-transport-limited (MTL) regime), or as a reaction on the surface (the reaction-rate-limited (RRL) regime).²

We are using this reaction to examine the reactivities of surface alkyls on platinum under conditions representative of those employed in heterogeneous catalytic hydrogenations of olefins. This reaction is a valuable probe of mechanisms. It can generate surface alkyls (R*) derived from the R group in (COD)PtR₂ that (1) have C* bonds that are initially stereochemically well-defined (e.g., *n*-propyl* vs isopropyl* and *exo*-2-norbornyl* vs *endo*-2-norbornyl*),^{4,5} (2) have initially well-defined patterns of isotopic labeling (e.g., CH₃CD₂* vs CD₃CH₂*), and (3) cannot be derived from the hydrogenations of olefins (e.g., R = methyl, neopentyl, phenyl, 1-norbornyl).

In previous studies of the reductions of (COD)PtR₂ complexes and of olefins, we used aprotic solvents (most commonly *n*-heptane). Interpretation of the isotopic distributions of deuterated

(1) The National Science Foundation (Grant CHE-88-12709), the Office of Naval Research, and the Defense Advanced Research Projects Agency supported this work.

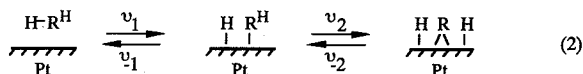
(2) Miller, T. M.; Izumi, A. N.; Shih, Y.-S.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 3146-3156.

(3) Miller, T. M.; McCarthy, T. J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 3156-3163.

(4) Miller, T. M.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 3164-3170.

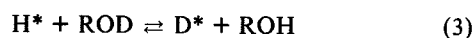
(5) Lee, T. R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1991**, *113*, 368-369.

alkanes produced from these reductions was difficult for four reasons.^{3,4} First, isotopic exchange (the extent of which was difficult to quantify) occurred between H(D)* and H₂ (or D₂). Second, exchange of H/D occurred between the surface alkyls derived from the platinum complex and the aprotic solvent by activation of the C-H bonds of the solvent (eq 2, ν_1). Third,



transfer of H/D occurred between the surface alkyls derived from the diolefin and the R groups via C-H bond activation of the type shown in step 2 of eq 2. Fourth, the fraction of deuterium atoms on the surface ($F_D = D^*/(D^* + H^*)$) in reductions by D₂ was probably different for R* moieties derived from (COD)PtR₂ complexes and from olefins: that is, the local concentration of H* near R* moieties derived from the complexes was probably higher than that near R* moieties derived from olefins (vide infra).

In order to simplify this system, we have conducted the reductions of (COD)PtR₂ complexes in protic solvents. In the reductions of olefins on platinum black in protic solvents, the product alkanes contained the isotope from the solvent (ROH or ROD) rather than from the gas (H₂ or D₂).^{6,7} We inferred from this result that the exchange of H/D between the protic solvent and the hydrides on the surface of the catalyst (eq 3)⁸⁻¹¹ was more rapid than the reductive elimination of the alkyl from the surface. The exact mechanism of this isotopic exchange is not well established.^{6,7}



In the present study, we have used the rapid isotopic exchange of hydrogen between the protic solvent and the surface of the catalyst to determine the predominant isotopic species on the surface of the catalyst (H* or D*, dictated by ROH or ROD). By ensuring complete equilibration of H* with ROD, we simplify the study of the reactions of surface alkyls by largely (or completely) eliminating three processes of isotopic exchange that complicated previous studies: between H(D)* and H₂ (or D₂), between the coadsorbed diolefin* and R* moieties, and between the surface alkyls and the C-H bonds of the solvent. We also ensure that surface alkyls derived from (COD)PtR₂ and those derived independently from olefins react with pools of H(D)* that have the same isotopic compositions.

The paper addresses some unresolved questions concerning the mechanism of the reduction of (COD)PtR₂ complexes by H₂ on platinum black. What are the reactivities of the surface-alkyl moieties; particularly, what are the relative rates of interchange of hydrogen between R* and H(D)*, and of conversion of R* to R-H(D) by reductive elimination? Do surface alkyls (R*) generated by the reduction of (COD)PtR₂ complexes differ from those generated by the hydrogenation of olefins (R^(-H))*? Do the surface alkyls derived from the diolefin and the R groups interact with one another during the course of the reaction?

We addressed these questions using the following strategy. We defined kinetic regimes (MTL and RRL) for the reductions of *cis*-cyclooctene and of (COD)PtMe₂ in ethyl alcohol. We established, under both MTL and RRL conditions, the influence of the protic solvent on the isotopic compositions of the product alkanes. In both kinetic regimes, using EtOD as solvent, we compared the distributions of products (ethanes-*d_n* and cyclooctanes-*d_n*) from the reductions of (COD)PtEt₂ with those from reductions of COD and of ethylene.¹² Finally, we compared the

distributions of propanes-*d_n* produced from the reductions in EtOD under RRL conditions of (COD)Pt(*n*-propyl)₂ and of CODPt-(isopropyl)₂ to that produced by the reduction of propylene under similar conditions.

Experimental Section

General Procedures. Ethyl alcohol (USI, absolute) and ethyl alcohol-*d* (Aldrich, 99.5+ atom % D) were deoxygenated by purging with argon, and stored under argon. We purchased *n*-heptane (99.9%, HPLC grade, SureSeal bottle) from Aldrich, and stored it under argon. The volumes of solvents used in reductions were measured and transferred with gas-tight syringes. Platinum black (Aldrich, Lot Nos. 10410HT and 03019KT) and dichloro(1,5-cyclooctadiene)platinum(II) ((COD)PtCl₂, Johnson Matthey Inc.) were used as received. The substrates *cis*-cyclooctene (Wiley, 99.9%) and 1,5-cyclooctadiene (COD, Aldrich, 99+%) were passed through silica immediately before use. Dihydrogen and 10% dihydrogen in argon were the highest purity available from Matheson, and were passed through Radox (Fisher Scientific) and activated molecular sieves before use. Ethylene, propylene, and D₂ (Matheson) were used without purification. A 10% dideuterium in argon mixture was prepared for use in reductions in the MTL regime by evacuating a 10-L gas cylinder, filling it with 1 atm of dideuterium, and pressurizing it with argon to 150 psig.

We conducted the reductions in 20-mL pressure-bottle reactors (Lab Glass; silanized as described previously²). For reductions under RRL conditions, the neoprene septa used to cap the bottles were used as received from Lab Glass; under MTL conditions, they were extracted with methylene chloride, and rinsed with ethyl alcohol before use. We controlled reaction temperatures to ± 1 °C by immersing the reactors to within ~ 1 cm of their metal crown caps in a large bath of water/ethylene glycol (1:1, v/v) thermostated by a Neslab Cryocool ($T < 0$ °C) or a Fisher circulating bath ($T > 0$ °C). We generated the low pressures of H₂ (or D₂) required for MTL conditions by using 10% H₂(D₂) in argon mixtures. Dihydrogen (or dideuterium) and 10% H₂(D₂) in argon mixtures were admitted to the reactors via syringe needles inserted through the septa of the reactors. We measured the pressures inside the reactors by inserting a syringe needle equipped with a pressure gauge through the septa; these pressures are probably accurate to $\pm 5\%$. Since the headspace of the reactors did not contain enough H₂ (or D₂) for complete reduction of the substrate under MTL conditions, these reductions were run with slow leaks (~ 5 mL/min of gas) of gas from the reactors. The leaks provided a constant pressure of H₂ (or D₂) over the solution, and were regulated by a fine-metering valve (Nupro) connected to a syringe needle inserted through the septa of the reactors. Stirring rates (the number of revolutions per minute (RPM) of the football-shaped (10 \times 6 mm) magnetic stir bar) were determined by use of a calibrated strobe light.

We measured ¹H NMR spectra at 250 or 300 MHz. Gas chromatograms were obtained with use of a 5% SE-30 capillary column. We measured the UV absorbances of aliquots from kinetics runs on a Gilford 240 single-beam spectrophotometer. Determinations of the surface areas of platinum black involved dihydrogen-dioxygen titrations, and have been described previously.² Mass spectra were obtained with a Hewlett-Packard 5992A GC/MS (70-eV electron-impact ionization) with use of the software for Selected Ion Monitoring from Hewlett-Packard. Methanes, ethanes, and propanes were analyzed using a 2-m Apiezon column, and cyclooctanes were analyzed with use of a 2-m SE-30 column.

We used platinum black (which we refer to as cat2) from a different supplier than that (cat1) used in our earlier studies of the reductions of (DO)PtR₂ complexes.²⁻⁴ The surface area of cat2, 0.50 ± 0.06 $\mu\text{g-atom/mg Pt black}$ (the value shown represents the platinum atoms accessible by dihydrogen-dioxygen titration²) was 80% higher than that of cat1, 0.28 ± 0.05 $\mu\text{g-atom/mg Pt black}$. Thus, for equivalent amounts of catalyst, the rates of reductions in *n*-heptane under RRL conditions were faster on cat2 than on cat1.² The reactivities of surface alkyls (as measured by the interchange of H/D between coadsorbed alkyl species) was, however, indistinguishable on the two catalysts (vide infra).

Synthesis of Substrates. The platinum complexes (1,5-cyclooctadiene)dimethylplatinum(II) ((COD)PtMe₂),¹³ (1,5-cyclooctadiene)diethylplatinum(II) ((COD)PtEt₂),¹⁴ (1,5-cyclooctadiene)di-*n*-propylplatinum(II) ((COD)Pt(*n*-Pr)₂),⁴ (1,5-cyclooctadiene)diiso-

(6) Lee, T. R.; Whitesides, G. M. *J. Am. Chem. Soc.* **1991**, *113*, 369-370.

(7) Lee, T. R.; Whitesides, G. M. *J. Am. Chem. Soc.* **113**, previous paper in this issue.

(8) Bond, G. C. *Catalysis by Metals*; Academic Press: London, 1962; pp 217-221.

(9) McDaniel, E. L.; Smith, H. A. *Adv. Catal.* **1957**, *9*, 76-83.

(10) Philipson, J. J.; Burwell, R. L., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 6125-6133.

(11) McNaught, W. G.; Kemball, C.; Leach, H. F. *J. Catal.* **1974**, *34*, 98-105.

(12) We published an early report on this subject: McCarthy, T. J.; Shih, Y.-S.; Whitesides, G. M. *Proc. Nat. Acad. Sci. U.S.A.* **1981**, *78*, 4649-4651. The conclusions presented in this paper were oversimplified for two reasons: the relative abundances of values of *m/e* in the mass spectra of mixtures of ethanes-*d_n* were interpreted as the relative abundances of isotopomers,⁷ and kinetic regimes (e.g., MTL vs RRL) were not defined.

(13) Kristner, C. R.; Hutchison, J. H.; Doyle, J. R.; Storlie, J. C. *Inorg. Chem.* **1963**, *2*, 1255-1261.

(14) Brainard, R. L.; Whitesides, G. M. *Organometallics* **1985**, *4*, 1550-1557.

Table I. Standard Conditions for the Reductions of (COD)PtMe₂ and of *cis*-Cyclooctene

parameter	MTL	RRL	remarks
(COD)PtMe ₂ (mg; μmol)	18; 54	15; 45	kinetics studies
	15–20; 45–60	15–20; 45–60	isotopic studies
<i>cis</i> -cyclooctene (mg; μmol)	30; 270	60; 550	kinetics studies
	15; 140	15; 140	isotopic studies
solvent (mL)	3	3	ethyl alcohol or <i>n</i> -heptane
vessel (mL)	20	20	glass pressure tube
<i>P</i> _{H₂} (atm)	0.17	2.4	
<i>T</i> (°C)	40	–20	
catalyst (mg)	40	30	platinum black
<i>S</i> _{Pt} (μg-atom) ^a	20	15	established by H ₂ /O ₂ titration
stirring (rpm)	1800	1800	rate of rotation of football-shaped magnetic stir bar (10 × 6 mm)
analysis	GC, UV GC/MS	GC, UV GC/MS	kinetics studies isotopic studies

^a Values of *S*_{Pt} represent absolute surface areas for a given amount of catalyst.

propylplatinum(II) ((COD)Pt(*i*-Pr)₂)¹⁵ (dicyclopentadiene-*d*₁₂)dimethylplatinum(II) ((DCPD-*d*₁₂)PtMe₂)³ and (1,5-cyclooctadiene)dimethylplatinum(II) ((COD)Pt(CD₃)₂)⁴ were prepared with yields of 60–75% by use of established literature procedures. The ¹H NMR spectra of these compounds were consistent with those reported in the literature. We give a representative synthesis for (COD)PtMe₂.

In a 100-mL Schlenk flask equipped with a magnetic stir bar, a suspension of 0.702 g (1.88 mmol) of (COD)PtCl₂ in diethyl ether (50 mL) was cooled to –78 °C under an atmosphere of argon. A 1.15 M solution of methylmagnesium bromide (3.7 mL, 4.3 mmol) in diethyl ether was added dropwise via cannula. The solution was stirred and allowed to warm slowly to 0 °C. Analysis by thin-layer chromatography (1:1, pentane/diethyl ether) showed the reaction to be complete. Methyl alcohol (1 mL) was added slowly to quench excess Grignard reagent. The solution was filtered through a glass frit with liberal washing of the solids with pentane. The filtrate was washed through a plug of silica gel, and concentrated to dryness by rotary evaporation. The resulting white solid was purified by chromatography on silica gel (10:1, pentane/diethyl ether), yielding 0.425 g (68%) of (COD)PtMe₂. No further purification was needed to obtain reproducible kinetic data.

Kinetics of Reductions: General Methods. The standard conditions for kinetics experiments are given in Table I. A reaction vessel equipped with a magnetic stir bar was charged with catalyst, capped, purged for ~10 min with argon, and placed in the constant-temperature bath. A 1-mL portion of solvent (ethyl alcohol or *n*-heptane) was added to the catalyst by syringe, and stirring was started. The vessel was purged with H₂ (or 10% H₂/Ar) for 30 s, and then held at constant pressure for 10 min. Meanwhile, the substrate was dissolved in 3 mL of solvent under argon in a 1-dram vial capped with a rubber septum. After 10 min, stirring was stopped; the catalyst was allowed to settle to the bottom of the reactor, and the solvent was carefully removed via cannula. The atmosphere over the substrate was purged with H₂ (or 10% H₂/Ar) for 10 s after which the substrate was admitted to the reactor via cannula under a pressure of H₂ (or 10% H₂/Ar). An aliquot was removed (*t* = 0).¹⁶ Stirring was resumed; simultaneously, a stopwatch was started. Aliquots were removed periodically, and worked up as described in the following text. During a typical run, 6–8 aliquots (averaging 75 μL each) were taken; consequently, ca. 15% of the total volume of solution was removed.

For reductions of (COD)PtMe₂, the aliquots were diluted in air by a factor of 100 by transferring 50 μL (using a 50-μL disposable glass micropipet) to a 5-mL volumetric flask, and filling to the mark with the solvent used in the reduction. The sample was transferred to a 3.0-mL quartz cuvette (10 × 10 × 30 mm), and the UV absorbance was measured at 290 nm.² The amount, *n_t* (μmol), of (COD)PtMe₂ present at time *t* was calculated using eq 4, where *A_t* is the absorbance of the solution at time *t*.

$$n_t((\text{COD})\text{PtMe}_2) = n_0((\text{COD})\text{PtMe}_2)(A_t/A_0) \quad (4)$$

For reductions of *cis*-cyclooctene, the aliquots were withdrawn and directly analyzed by capillary GC. Since the response factors for *cis*-cyclooctene and cyclooctane were indistinguishable, no internal standard was necessary. The amount, *n_t* (μmol), of *cis*-cyclooctene present at time *t* was calculated using eq 5, where *A_{t,s}* (*s* denotes substrate) is the integrated area for *cis*-cyclooctene, and *A_{t,p}* (*p* denotes product) is the integrated area for cyclooctane at time *t*.

$$n_t(\text{cis-cyclooctene}) = n_0(\text{cis-cyclooctene})(A_{t,s}/(A_{t,s} + A_{t,p})) \quad (5)$$

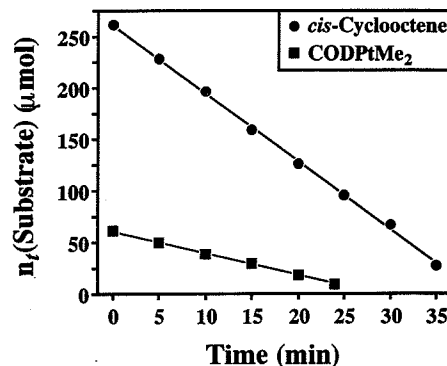


Figure 1. Kinetics of the reductions under MTL conditions of *cis*-cyclooctene and of (COD)PtMe₂. The plots show zero-order dependence on the concentrations of the substrates. The rate of reduction of *cis*-cyclooctene is 3 times that of (COD)PtMe₂, as expected on the basis of the number of equivalents of hydrogen consumed in the reduction of each.

Isotopic Labeling Experiments: General Methods. Table I gives the standard conditions employed in the isotopic labeling experiments. For reductions of both the platinum complexes and COD, we used the procedure outlined previously for kinetic runs, but without stopping the reactions to remove aliquots. For reductions of ethylene and of propylene, we used the following procedure. A reaction vessel equipped with a magnetic stir bar was charged with catalyst, capped, purged for ~10 min with argon, and placed in the constant-temperature bath. Solvent (ethyl alcohol or *n*-heptane, 1 mL) was added to the reactor by syringe, and stirring was initiated. The reactor was purged for 30 s with H₂ or D₂ (under RRL conditions), or 10% H₂/Ar or 10% D₂/Ar (under MTL conditions), and held at constant pressure for 10 min. After 10 min, stirring of the catalyst was stopped. The catalyst was allowed to settle, and the solvent was carefully removed via cannula. We added an additional 3 mL of solvent by syringe, and then 1 mL (at 1 atm) of ethylene or propylene gas by gas-tight syringe. We allowed sufficient time for all reactions to reach completion based on the rates measured for reductions of (COD)PtMe₂ and *cis*-cyclooctene: the reductions performed under MTL conditions were stopped after 30 min, and those conducted under RRL conditions were stopped after 1 h. In all cases, we observed complete conversion to products in the allotted times.

Isotopic Analysis of Alkanes-*d_n*. We have previously described in detail the procedures for determining the isotopic compositions of methanes-*d_n*,³ ethanes-*d_n*,⁷ propanes-*d_n*,⁴ and cyclooctanes-*d_n*.⁷ These procedures were used without modification in the work reported here. We use the average content of deuterium, *d_{av}* (eq 6), to describe the isotopic compositions of the alkanes-*d_n* produced in the reductions. We believe that values of *d_{av}* are accurate to ±5% absolute.

$$d_{av} = 1/100 \sum_{n=1}^m n(\% \text{ alkane-}d_n) \quad (6)$$

Results

Kinetics in the MTL Regime. Figure 1 summarizes the reductions of (COD)PtMe₂ and of *cis*-cyclooctene in ethyl alcohol. Both reactions are kinetically zero order in substrate. This behavior is typical of heterogeneous hydrogenations of olefins, and is generally interpreted to mean that all active sites on the surface

(15) Muller, J.; Goser, P. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 364–365.

(16) In ref 2, we described in detail the procedure for removing aliquots.

Table II. Rates of Reduction of (COD)PtMe₂ and of *cis*-Cyclooctene over Platinum Black^a

substrate	solvent	catalyst ^b	MTL rate (μmol/min)	RRL	
				rate (μmol/min)	areal rate (μmol/min·S _{Pt})
(COD)PtMe ₂	<i>n</i> -heptane	1	3.9	0.96	0.11
<i>cis</i> -cyclooctene			(12) ^c	58	6.6
(COD)PtMe ₂		2		2.5	0.16
<i>cis</i> -cyclooctene				93	6.2
(COD)PtMe ₂	ethyl alcohol		1.9	0.65	0.043
<i>cis</i> -cyclooctene			6.0	36	2.4

^a We estimate the error in the rates (μmol/min) to be ±15% or less. ^b The results using cat1 are taken from ref 2. ^c This value is that obtained for the reduction of 1-octene rather than that of *cis*-cyclooctene. We believe that *cis*-cyclooctene and 1-octene reduce at the same rate under these conditions.

of the catalyst are saturated with surface alkyl groups.¹⁷⁻²² We propose that this interpretation also applies to the reductions of (COD)PtMe₂ and of *cis*-cyclooctene reported here. The rate of reduction of *cis*-cyclooctene was 3 times that of (COD)PtMe₂ (eq 7). Since the conversion of *cis*-cyclooctene to cyclooctane requires

$$dn_i(\text{cis-cyclooctene})/dt = 3 dn_i((\text{COD})\text{PtMe}_2)/dt \quad (7)$$

1 equiv of H₂, and the conversion of (COD)PtMe₂ to alkanes requires 3 equiv of H₂, the ratio of rates in eq 7 indicates that diffusion of dihydrogen to the catalyst surface in these two reactions was rate-limiting. Previously, we observed this ratio of rates for reductions under MTL conditions of 1-octene and (COD)PtMe₂ in *n*-heptane.²

The rates of reduction for (COD)PtMe₂ and *cis*-cyclooctene under MTL conditions are presented in Table II. We showed previously that under MTL conditions, the rate of reduction of (COD)PtMe₂ in *n*-heptane does not increase with the absolute surface area of the catalyst (S_{Pt}, given in μg-atom) when S_{Pt} > 8.5 μg-atom.² Since the absolute surface area of cat2 under MTL conditions (S_{Pt} = 20 μg-atom for 40 mg of platinum black) was greater than 8.5 μg-atom by more than a factor of 2, the rates of reductions in *n*-heptane on cat1 and cat2 were probably the same under MTL conditions. The data in Table II indicate, therefore, that the rates of reduction in the MTL regime were slower in ethyl alcohol than those in *n*-heptane by a factor of ca. 0.5. The relative rates correlate with the relative solubilities of H₂ in the two solvents:^{21,22} the solubility of H₂ in ethyl alcohol at 40 °C is 1.82 × 10⁻³ mol H₂/mL solvent and that in *n*-heptane at 40 °C is 2.43 × 10⁻³ mol H₂/mL solvent.²³⁻²⁶ The origin of this correlation is ambiguous (vide infra).

Kinetics in the RRL Regime. Zero-order kinetics were also observed for the reductions of (COD)PtMe₂ and of *cis*-cyclooctene in ethyl alcohol under RRL conditions (Figure 2). As under MTL conditions, we interpret zero-order dependence on the concentration of substrate to mean that the surface is saturated with alkyl groups.¹⁷⁻²² Doubling the rate of rotation of the magnetic stir bar from 1800 to 3600 rpm in the reductions of (COD)PtMe₂ produced no observable change in the rate of reduction. This result indicates that the rate of reduction of (COD)PtMe₂ was not affected by mass transport of hydrogen to the surface of the

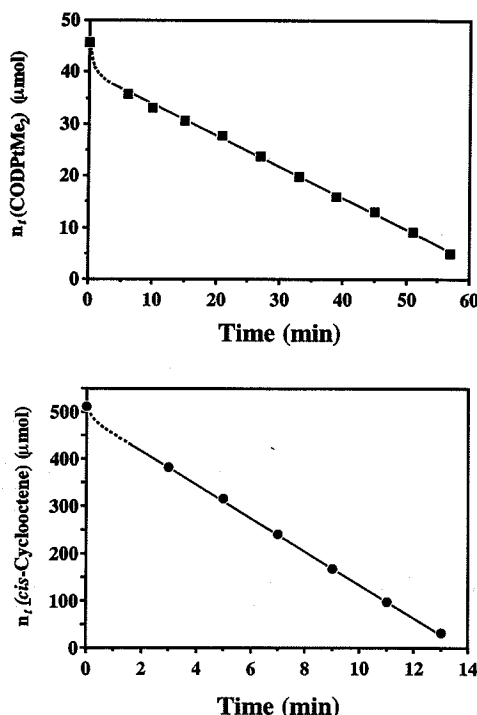


Figure 2. Kinetics of the reductions under RRL conditions of *cis*-cyclooctene (top) and of (COD)PtMe₂ (bottom). The plots show zero-order dependence on the concentrations of the substrates.

catalyst.¹⁸⁻²¹ We believe therefore that the rate of reduction was limited by a reaction on the surface.²

The reductions of (COD)PtMe₂ in ethyl alcohol under RRL conditions appear to show burst kinetics (Figure 2). The bursts for similar reductions of *cis*-cyclooctene were less substantial, but detectable. In a previous study, we observed apparent burst kinetics in the reductions under RRL conditions of (COD)PtMe₂ in *n*-heptane.² We suggested that the bursts resulted from the reaction of (COD)PtMe₂ with an initially hydride-rich surface of platinum. Since we did not observe burst kinetics under MTL conditions (either in this study or in the previous one), we now believe that the suggestion that the bursts result from the reaction of the complex with an initially hydride-rich surface is incorrect: if anything, the bursts should be more readily detected in the MTL regime (where the initial surface of platinum is certainly more hydride-rich than it is during the reduction) than in the RRL regime.

We hypothesized that the bursts resulted from experimental artifact: the solution containing the substrate was held at room temperature until it was admitted to the reactor via cannula; the burst kinetics therefore arose from an initially faster rate of reduction that slowed as the solution cooled from ca. 25 to -20 °C. To test this hypothesis, we performed a typical reduction of (COD)PtMe₂ in *n*-heptane, but cooled the solution to -30 °C before admitting it to the reactor. We observed no burst in the rate of reduction. We believe therefore that the burst kinetics are due to experimental artifact rather than reaction of the

(17) Webb, G. In *Comprehensive Chemical Kinetics*; Bamford, C. H., Tipper, C. F., Eds.; Elsevier: New York, 1978; Vol. 20, pp 1-121.

(18) Hussey, A. S.; Keulks, G. W.; Nowack, G. P.; Baker, R. H. *J. Org. Chem.* **1968**, *33*, 610-616.

(19) Kung, H. H.; Pellet, R. G.; Burwell, R. L., Jr. *J. Am. Chem. Soc.* **1976**, *98*, 5603-5611.

(20) Price, R. H.; Schiewetz, D. B. *Ind. Eng. Chem.* **1957**, *49*, 807-812.

(21) Madon, R. J.; O'Connell, J. P.; Boudart, M. *AIChE J.* **1978**, *24*, 904-911.

(22) Boudart, M.; Djega-Mariadassou, G. *Kinetics of Heterogeneous Catalytic Reactions*; Princeton University: Princeton, N.J., 1984; pp 180-187.

(23) We derived these values of solubility by taking the values of solubility at 40 °C given in mL H₂/g solvent²⁴ and converting them to mol H₂/mL solvent using the density at 40 °C of *n*-heptane²⁵ and ethyl alcohol,²⁶ and 22.414 L/mol as the standard molar volume of H₂.

(24) *Losungsgleichgewichte I*; Schafer, K., Lax, E., Eds.; Landolt-Bornstein, 6th ed., Bandteil b; Springer-Verlag: Berlin, 1962; p 70.

(25) *Gleichgewichte Dampf-Kondensat Osmotische Phänomene*; Schafer, K., Lax, E., Eds.; Landolt-Bornstein, 6th ed., Bandteil a; Springer-Verlag: Berlin, 1960; p 197.

(26) Maxted, E. B.; Moon, C. H. *Trans. Faraday Soc.* **1936**, *32*, 769-775.

Table III. Isotopic Compositions (d_{av}) of the Alkanes Produced in the Reductions of (DCPD- d_{12})Pt(CH₃)₂ and of (COD)Pt(CD₃)₂ in Ethyl Alcohol and in *n*-Heptane^a

complex	solvent	MTL		RRL	
		methanes	cyclooctanes	methanes	cyclooctanes
(DCPD- d_{12})Pt(CH ₃) ₂	<i>n</i> -heptane	0.50 ± 0.04		0.04 ± 0.01	
	EtOH	0.00 ± 0.00		0.00 ± 0.00	
(COD)Pt(CD ₃) ₂	<i>n</i> -heptane	2.13 ± 0.03	1.25 ± 0.01	2.71 ± 0.02	0.07 ± 0.00
	EtOH	2.52 ± 0.03	0.01 ± 0.00	2.81 ± 0.02	0.00 ± 0.00

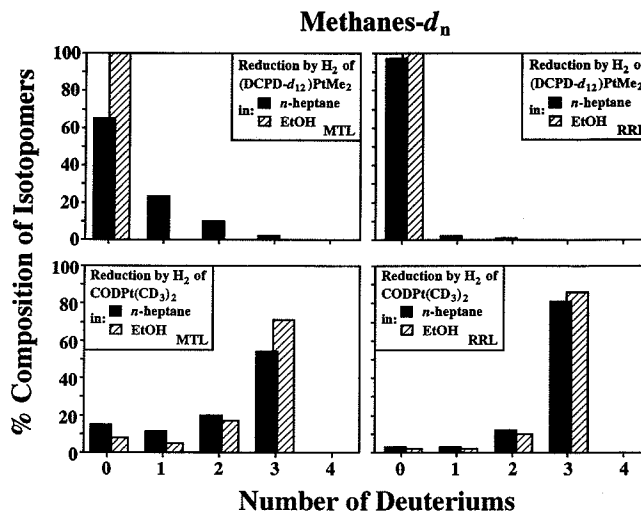
^a The value indicated by ± is the difference between duplicate runs.

substrates with a hydrogen-rich surface of platinum.

The observation of less substantial bursts for reductions of *cis*-cyclooctene than for reductions of (COD)PtMe₂ probably reflects a lower activation energy for the reduction of *cis*-cyclooctene than that for the reduction of (COD)PtMe₂.²⁷ We did not observe burst kinetics in the MTL regime, presumably because the reactor was held above room temperature (40 °C). In addition, we did not observe an induction period under MTL conditions, nor would we expect to: the activation energy for diffusion in solvents of normal viscosity is small ($E_a < 5$ kcal/mol);^{28,29} therefore, the rate of reduction should not vary substantially with a small change in temperature ($\Delta T \approx 15$ °C).

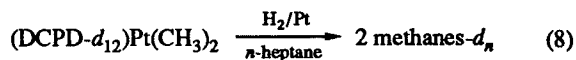
The data in Table II show that, in the RRL regime, the rates of reduction of (COD)PtMe₂ and *cis*-cyclooctene were slower in ethyl alcohol than in *n*-heptane. Under these conditions, dihydrogen is more soluble in *n*-heptane than in ethyl alcohol.³⁰ Boudart and co-workers proposed that for heterogeneous hydrogenations of olefins in the liquid phase (under conditions in which transfer of H₂ from the gas to the liquid phase was *not* rate-limiting), the relative rates of reduction in various solvents depend on the relative concentrations of dissolved H₂ in the solvents.^{21,22} This proposal assumed, however, that the rate-determining step in heterogeneous hydrogenations of olefins is the adsorption of H₂ on the surface of the catalyst. Since the rate-determining step(s) of this reaction has (have) not, in our opinion, been unambiguously identified, we regard their proposal as premature.³¹ In any event, the ratio of rates (rate in *n*-heptane/rate in ethyl alcohol) for *cis*-cyclooctene was 2.6 ± 0.9 , and that for (COD)PtMe₂ was 3.8 ± 1.5 . These two ratios agree within experimental error, and suggest that the factors responsible for the correlations between the rates of reduction and the solubility of H₂ in the solvent are the same for reductions of olefins and of (COD)PtR₂ complexes.

In Table II, the kinetic data from reductions under RRL conditions of (COD)PtMe₂ and *cis*-cyclooctene in *n*-heptane on cat1 and cat2 show that the rates of reduction of (COD)PtMe₂ were faster on cat2 than on cat1 (2.5 vs 0.96 $\mu\text{mol}/\text{min}$); the rate increased linearly (within experimental error) with the increase in surface area: the areal rate (rate per unit surface area) obtained with use of cat2 ($0.16 \pm 0.06 \mu\text{mol}/\text{min} \cdot S_{\text{Pt}}$) agreed within experimental error to that obtained with use of cat1 ($0.11 \pm 0.04 \mu\text{mol}/\text{min} \cdot S_{\text{Pt}}$). In addition, the rates of reduction of *cis*-cyclooctene in *n*-heptane were also faster on cat2 than cat1 (93 vs 58 $\mu\text{mol}/\text{min}$); within experimental error, the areal rate increased

**Figure 3.** Isotopic distributions of the methanes- d_n produced from the reductions by H₂ of (DCPD- d_{12})PtMe₂ (top) and (COD)Pt(CD₃)₂ (bottom) in *n*-heptane and EtOH under MTL (left) and RRL (right) conditions.

linearly with the surface area of platinum (6.2 ± 1.9 vs $6.6 \pm 2.8 \mu\text{mol}/\text{min} \cdot S_{\text{Pt}}$). These results indicate that diffusion of hydrogen was not rate-limiting for reductions of (COD)PtMe₂ and *cis*-cyclooctene in *n*-heptane under RRL conditions.^{18–21} The slower rates of reduction of these substrates in ethyl alcohol than in *n*-heptane argue that the rates of reductions in ethyl alcohol under RRL conditions were also not limited by mass-transport of hydrogen.

Transfer of deuterium from (DCPD- d_{12})* to CH₃* in *n*-heptane is greater under MTL than under RRL conditions. No transfer occurs in EtOH. We investigated the efficiency of transfer of deuterium from diolefin* moieties to R* moieties by examining the isotopic compositions of the methanes- d_n produced in the platinum-catalyzed reductions of (DCPD- d_{12})Pt(CH₃)₂ in *n*-heptane (eq 8; Table III). In eq 8, we have included the data



D transferred to CH₃* from (DCPD- d_{12})*

	cat2	cat1 ³
MTL	0.50	0.49
RRL	0.04	0.05

from ref 3 for the reductions of this substrate on cat1 in order to demonstrate that the reactivities of the surface alkyls were similar on both catalysts within each kinetic regime. We used (DCPD- d_{12})Pt(CH₃)₂ rather than (COD- d_{12})Pt(CH₃)₂ because DCPD was easier to obtain in perdeuterated form. These data indicate that, in *n*-heptane, the transfer of deuterium from diolefin* moieties to R* moieties occurred under both MTL conditions and (albeit to a significantly lesser extent) under RRL conditions. Reductions of this substrate in EtOH (Figure 3; Table III) showed, in both kinetic regimes, *no* transfer of deuterium. We believe that

(27) In ref 2, we observed under RRL conditions in *n*-heptane an activation energy of 8.3 ± 0.6 kcal/mol for reductions of COD, and an activation energy of 15 ± 2 kcal/mol for reductions of (COD)PtMe₂.

(28) Benson, S. W. *The Foundations of Chemical Kinetics*; McGraw-Hill: New York, 1960; p 499.

(29) Shooter, D. In *Comprehensive Chemical Kinetics*; Bamford, C. H., Tipper, C. F., Eds.; Elsevier: New York, 1969, Vol. 1, p 253.

(30) We could not obtain data for the relative solubilities of H₂ in *n*-heptane and in ethyl alcohol at -20 °C, but we found (in a manner analogous to that described in ref 23) that at 0 °C the solubility in *n*-heptane is 2.01×10^{-3} mol H₂/mL solvent, and that in ethyl alcohol is 1.56×10^{-3} mol H₂/mL solvent.

(31) The *only* scenario in which the rates of reduction can *depend* on the solubility of H₂ in the solvent *requires* adsorption of H₂ as the rate-determining step—a possibility under RRL conditions, an impossibility under MTL conditions. Certainly the rates (under *both* RRL and MTL conditions) correlate with the solubilities of H₂ in the solvents, but inferring dependence from correlation is imprudent. In the solvents we studied, it seems possible that the occupation of coordination sites by ethyl alcohol might slow rates of reduction in that solvent relative to those in *n*-heptane.

(32) The CD₃I that we used to synthesize (COD)Pt(CD₃)₂ (via CD₃MgI addition to (COD)PtCl₂) was 99 atom % D. The maximum content of deuterium in the methanes was therefore 2.97 D rather than 3.00 D.

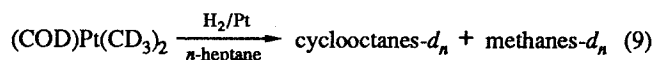
Table IV. Isotopic Compositions (d_{av}) of the Alkanes Produced in the Reductions of (COD)PtEt₂, of COD, and of Ethylene in Ethyl Alcohol^a

substrate		MTL			RRL		
		D ₂ /EtOD	H ₂ /EtOD	D ₂ /EtOH	D ₂ /EtOD	H ₂ /EtOD	D ₂ /EtOH
(COD)PtEt ₂	cyclooctanes	14.8 ± 0.1	14.6 ± 0.0	0.06 ± 0.01	8.9 ± 0.8	8.4 ± 0.4	0.9 ± 0.5
COD		13.2 ± 0.2	12.6 ± 0.2	0.44 ± 0.02	5.7 ± 0.0	4.5 ± 1.6	0.23 ± 0.03
(COD)PtEt ₂	ethanes	1.8 ± 0.2	1.8 ± 0.1	0.00 ± 0.00	1.2 ± 0.1	1.0 ± 0.1	0.05 ± 0.01
Ethylene		4.2 ± 0.3	4.1 ± 0.1	0.5 ± 0.1	1.9 ± 0.0	1.3 ± 0.3	0.63 ± 0.02

^a The value indicated by ± is the difference between duplicate runs.

the absence of transfer in ethyl alcohol reflects the interception of D* by exchange with EtOH.

Transfer of deuterium from CD₃* to COD* in *n*-heptane is faster under MTL than RRL conditions. No transfer occurs in EtOH. We also investigated the efficiency of the reverse process—the transfer of deuterium from the R* moieties to the diolefin* moieties—by examining the isotopic compositions of the cyclooctanes- d_n and the methanes- d_n generated in the platinum-catalyzed reductions of (COD)Pt(CD₃)₂ by H₂ in *n*-heptane (eq 9;



D transferred to COD* per CD₃* D lost from CD₃*³²

MTL	0.63	0.84
RRL	0.04	0.26

Table III). These data are consistent with those in the preceding section and show that in *n*-heptane the transfer of deuterium from the R* moieties to the diolefin* moieties was greater under MTL conditions than under RRL conditions. The greater transfer of deuterium between coadsorbed surface species under MTL conditions than under RRL conditions probably results from faster rates of C–H bond activation (relative to the rates of reductive elimination as alkanes) of surface alkyls under MTL conditions than under RRL conditions.^{7,33}

The distribution of the isotopomers of methane from the reductions of (COD)Pt(CD₃)₂ by H₂ in *n*-heptane is given in Figure 3; no methane- d_4 was formed. This surprising observation suggests that transfer of deuterium did not occur between coadsorbed methyl moieties. Since transfer of deuterium occurs between CD₃* moieties and cyclooctyl* moieties, we hypothesize that the lack of exchange between coadsorbed methyl moieties results because H* generated by loss from cyclooctyl* groups overwhelms the local concentrations of H(D)* near the CD₃* groups (vide infra).

The reductions in EtOH (Figure 3; Table III) showed that, within experimental error, no transfer of deuterium from the R* moieties to the diolefin* moieties occurred under either MTL or RRL conditions. Again, the isotopic exchange of hydrogen between the surface of the catalyst and the protic solvent appears to be fast.

In the reductions of (COD)Pt(CD₃)₂ under MTL conditions, the surface methyls retain 2.5 D in ethyl alcohol, and 2.1 D in *n*-heptane. Since any D* produced by C–D bond activation of CD₃* is rapidly exchanged with the protic solvent,^{6,7} this observation suggests that the rate of C–D bond activation (relative to the rate of reductive elimination as methane) of CD₃* species was slower in ethyl alcohol than in *n*-heptane. There are at least two possible rationalizations for this result. First, if the mechanism

(33) In the reductions of (COD)Pt(CD₃)₂ by H₂ in *n*-heptane, the sum of isotopic exchange between (1) H₂ and D*, and (2) the hydrocarbon solvent and D* (which occurs via C–H bond activation of the solvent³) was similar in both kinetic regimes. The difference between the deuterium transferred per CD₃* group to cyclooctyl* groups and the deuterium lost from each CD₃* group reflects the net loss of D via these two routes. This value is 0.84–0.63 = 0.21 D under MTL conditions, and 0.26–0.04 = 0.22 D under RRL conditions. It is intriguing that the net loss of D is similar in these disparate kinetic regimes. We propose that for reductions in *n*-heptane, exchange between D* and the solvent is faster in the MTL regime than in the RRL regime—a statement we know to be true³—while exchange between D* and H₂ is faster in the RRL regime than in the MTL regime—a statement consistent with our earlier hypothesis that the rate of isotopic exchange between H* and D₂ is greater under RRL conditions than under MTL conditions.³ We believe therefore that the varying contributions from these two processes account for the similarity in the net loss of D in the two kinetic regimes.

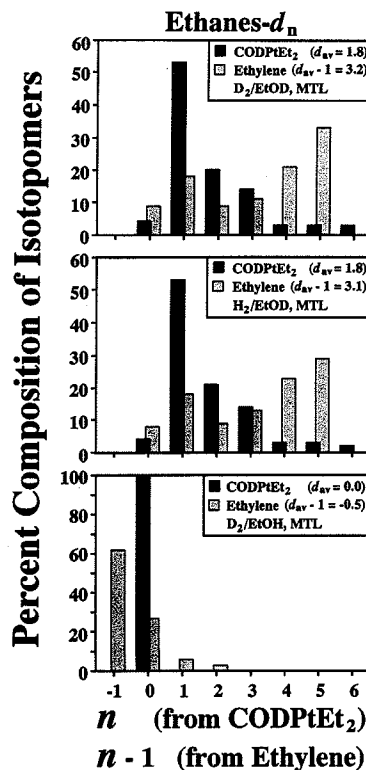


Figure 4. Isotopic distributions of the ethanes- d_n produced from the reductions of (COD)PtEt₂ and of ethylene using D₂/EtOD (top), H₂/EtOD (middle), and D₂/EtOH (bottom) under MTL conditions (n = number of deuteriums).

of the reduction of (COD)PtR₂ complexes proceeds predominantly by reductive elimination of R* prior to reductive elimination of cyclooctyl* (vide infra), then the generation of H* by loss from the cyclooctyl* moieties could result in rapid reductive elimination of the coadsorbed CD₃* moieties. A higher flux³⁴ of H* from cyclooctyl* to CD₃* in ethyl alcohol than in *n*-heptane³⁵ would correspond to a shorter residence time for the CD₃* moieties in ethyl alcohol. This shortened residence time might correlate with a smaller extent of C–D bond activation of the CD₃* moieties in ethyl alcohol than in *n*-heptane. Second, more deuterium might remain in the CD₃* moieties in ethyl alcohol than in *n*-heptane because the highly coordinating, polar solvent might retard C–D bond activation relative to the noncoordinating one. We prefer the latter explanation because, under MTL conditions, the rate of reduction of (COD)PtMe₂ is faster in *n*-heptane than in ethyl alcohol; as a result, the average residence time for surface alkyls is probably longer in ethyl alcohol than in *n*-heptane. This observation is probably inconsistent with the first explanation.

Under MTL conditions, the incorporation of deuterium into Et* and cyclooctyl* moieties differs significantly when these species

(34) Although the deuterium label is completely intercepted via exchange with the OH group of the solvent, the flux of hydrogen between these coadsorbed surface alkyl species is, however, probably not eliminated by ethyl alcohol.

(35) A higher flux in ethyl alcohol than in *n*-heptane could result from the addition of the O–H bond of the protic solvent to the surface of platinum generating EtO* + H*. It is possible that the rapid isotopic exchange of hydrogen between protic solvents and the surface of platinum occurs via this reaction.⁷

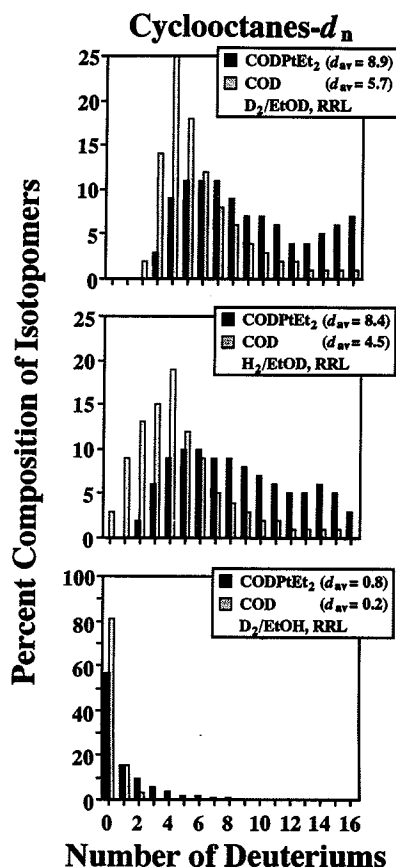


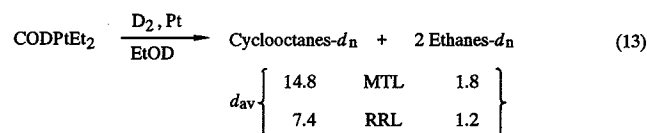
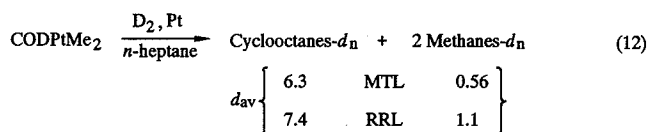
Figure 7. Isotopic distributions of the cyclooctanes- d_n produced from the reductions of (COD)PtEt₂ and of COD using D₂/EtOD (top), H₂/EtOD (middle), and D₂/EtOH (bottom) under RRL conditions.

(86%), and that from (COD)PtEt₂ was ethane- d_1 (73%). Thus, the relative rates of reductive elimination as ethane and exchange (hence, C-H bond activation) of surface ethyls generated under RRL conditions by the reductions of (COD)PtEt₂ and of ethylene appear to be similar. Fourth, the cyclooctanes from reductions of (COD)PtEt₂ using D₂/EtOD contained more deuterium than those derived from analogous reductions of COD ($d_{av} = 8.9$ vs 5.7). Again, as we observed under MTL conditions, the cyclooctyl* moieties from the complex appear to become more highly dehydrogenated than those from COD. Nevertheless, the additional H(D)* contributed by loss from cyclooctyl* moieties does not noticeably affect the coadsorbed Et* moieties under RRL conditions; this observation suggests that donation of H(D)* to an already H(D)*-rich surface is not significant.

Many of the data obtained here for reductions using D₂/EtOD are consistent with those obtained from similar reductions by D₂ in *n*-heptane.^{3,4,36} For example, in reductions by D₂ in *n*-heptane, the cyclooctanes produced from (COD)PtMe₂ ($d_{av} = 7.4$) contained more deuterium than those produced from COD ($d_{av} = 4.7$),³⁷ and the ethanes produced from (COD)PtEt₂ ($d_{av} = 1.2$) contained approximately one fewer deuterium than those produced

from ethylene ($d_{av} = 1.9$). In addition, the isotopic distribution of the ethanes- d_n generated from (COD)PtEt₂ appeared to be shifted by the omission of one deuterium relative to that generated from ethylene.

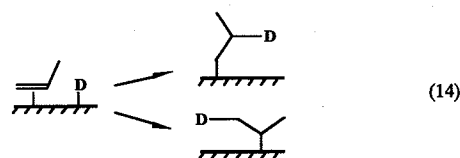
There are, however, mechanistically revealing differences between the reductions in *n*-heptane and those in EtOD. First, the reductions of (COD)PtMe₂ by D₂ in *n*-heptane produced cyclooctanes containing *less* deuterium under MTL conditions than under RRL conditions (eq 12);³ the reductions of this substrate



by D₂ in EtOD produced cyclooctanes containing substantially *more* deuterium under MTL conditions than under RRL conditions (eq 13; Table IV). Second, in reductions using D₂/*n*-heptane, the R* moieties generated from (COD)PtR₂ incorporated *less* deuterium under MTL conditions than under RRL conditions (eq 12),³ but in reductions using D₂/EtOD, the R* moieties incorporated *more* deuterium under MTL conditions than under RRL conditions (eq 13; Table IV). Both observations illustrate an important difference between solvents having and lacking exchangeable protons (or deuterons): for reductions in ROD, the rapid conversion of H* (generated by C-H bond activation of surface alkyls) to D* via exchange with ROD increases the content of deuterium in the product alkanes relative to that for reductions in solvents lacking exchangeable deuterons.

In the reductions of (COD)PtR₂ complexes by D₂ in *n*-heptane, the lesser content of deuterium in the alkanes produced under MTL conditions than under RRL conditions probably results because of a lower value of F_D for the former reductions. Values of F_D can plausibly vary with the reaction conditions in two ways. First, the markedly higher pressures of D₂ used in the RRL regime than in the MTL regime generate a higher concentration of D* under RRL conditions. The higher concentration of D* allows for rapid replacement of H* (by D*) via loss from the surface as HD (and possibly H₂). In contrast, the relatively low concentration of H(D)* under MTL conditions does not permit rapid replacement of H*; therefore, values of F_D are lower under MTL conditions than under RRL conditions. Second, activation of the C-H bonds of *n*-heptane (more extensive under MTL than under RRL conditions) lowers the values of F_D for reductions performed under MTL conditions.

Under RRL conditions, the distributions of isotopomers of propanes generated from the reductions by D₂ of (COD)Pt(*n*-Pr)₂ and (COD)Pt(*i*-Pr)₂ differ by one deuterium from that generated from the similar reduction of propylene. We compared the propanes obtained by reductions in EtOD of (COD)Pt(*i*-Pr)₂ and of (COD)Pt(*n*-Pr)₂ to those obtained by the analogous reduction of propylene (Figure 8). We wished to test the hypothesis that the isotopic distributions might permit us to distinguish the initial surface alkyl formed in the hydrogenation of propylene (eq 14).



If the reactivities (i.e., isotopic exchange) of either *n*-propyl* or isopropyl* were similar (or dissimilar) to that of propylene*, we might have been able to make this distinction. Although more deuterium was incorporated into the surface propyls derived from (COD)Pt(*i*-Pr)₂ ($d_{av} = 1.25$) than those derived from (COD)-

(36) The earlier studies in *n*-heptane were restricted to RRL conditions rather than MTL conditions for two reasons: to minimize the isotopic exchange of hydrogen via activation of the C-H bonds of the hydrocarbon solvent, and to generate the simplest possible distributions of alkanes- d_n by minimizing C-H(D) bond activation of the intermediate surface alkyls. In short, we wished to simplify interpretation of the data. These issues were not a concern in the present work due to the rapid exchange of H/D between the surface of the catalyst and EtOH(D).

(37) To explain this observation, we proposed that the concentration of D* was lower for reductions of COD than of (COD)PtMe₂.³ At present, we prefer an alternate explanation that is consistent with our observations of similar reductions in ethyl alcohol: the mechanism for the reduction of (COD)PtR₂ complexes in *n*-heptane involves a faster reductive elimination of R* moieties (possibly by H(D)* generated by the C-H bond activation of coadsorbed cyclooctyl* moieties) than of cyclooctyl* moieties; as a consequence, the cyclooctyl* moieties from (COD)PtR₂ become more highly dehydrogenated and thus more extensively deuterated upon reduction than those from COD.

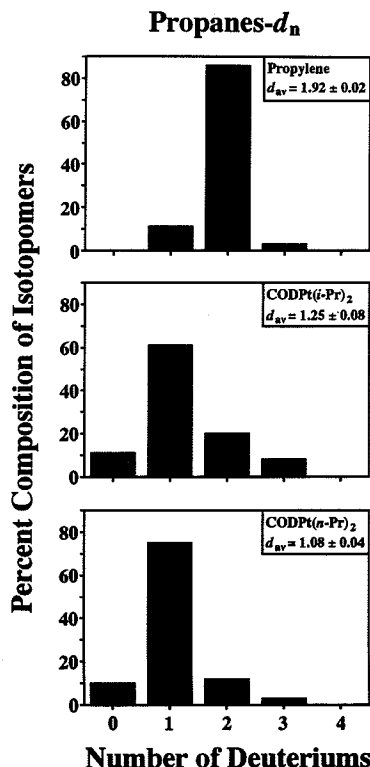


Figure 8. Isotopic distributions of the propanes- d_n produced from the reductions by D_2 of propylene (top), of (COD)Pt(*i*-Pr)₂ (middle), and of (COD)Pt(*n*-Pr)₂ (bottom) in ethyl alcohol- d under RRL conditions.

Pt(*n*-Pr)₂ ($d_{av} = 1.08$), this difference was not substantial enough to be diagnostic.³⁸

These data are, however, useful in demonstrating that, under RRL conditions, the propyl* moieties derived from the platinum complexes have relative rates of exchange and reductive elimination similar to those derived from propylene: the isotopic distributions of the propanes- d_n generated from the platinum complexes are similar to that, after correction for one additional deuterium atom, generated from propylene.³⁹

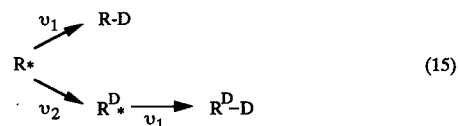
Discussion

The facile exchange of H/D between protic solvents and H(D)* provides a key to investigating the mechanism of heterogeneous hydrogenations of (DO)PtR₂ complexes. Our previous studies of the reductions of (DO)PtR₂ complexes and of olefins in alkane solvents were complicated particularly by the following: (1) the exchange of H/D between H(D)* and H₂ or D₂, (2) the inter-

change of H/D between the organic species present on the surface of the catalyst (a number of processes— α -hydride activation, β -hydride elimination, π -allyl formation, distal C–H bond activation—probably contributed to this interchange; the multiplicity of these processes made explicit observation of them difficult), and (3) the exchange of H/D between surface alkyls and the alkane solvent (via C–H activation of the solvent). All of these isotopic exchanges involved H(D)* as intermediates.

The fact that exchange between the pool of H(D)* and ROH(*D*) is virtually complete makes these problems tractable mechanistically.⁷ To a first approximation, all H* generated by loss from a surface alkyl is exchanged into the solvent, and disappears irreversibly from the system. Similarly, the only isotope of hydrogen present on the surface of the catalyst is D*, and thus the reduction of any C* bond must form a C–D rather than a C–H bond.

This facile conversion of C–H to C–D by exchange with the surface gives an easily measured reference reaction that we can use in characterizing surface alkyls. By examining the isotopic compositions of alkanes produced by the reductions of olefins or of (COD)PtR₂ complexes, we can measure the relative rates of the two pathways summarized in eq (15): irreversible reductive



elimination of the product alkane (ν_1), and (formally reversible) exchange of H/D with the surface (ν_2). The rate of exchange (ν_2) reflects the rate of C–H bond activation of the surface alkyl. A comparison of the relative rates of these processes gives us a way of characterizing and comparing surface alkyls prepared by different routes.

Under RRL conditions, the surface alkyls derived from the R group of (COD)PtR₂ complexes and from olefins seem to have similar reactivities; under MTL conditions, their reactivities are different. On the basis of the crude criteria we have available—the isotopic compositions of products of reductions in EtOD—it appears that surface alkyls (R*) produced by hydrogenation from olefins or by transfer to the surface from (COD)PtR₂ complexes are similar under RRL conditions. The isotopic distributions of the ethanes and of the propanes (Figures 6 and 8) provide examples.

Under MTL conditions, the R* moieties derived from the R group in (COD)PtR₂ produce differently isotopically substituted alkanes than those derived from an olefin in the only case we have examined: (COD)PtEt₂ vs ethylene. We emphasize that the observation that the isotopic distributions of ethanes obtained by MTL and RRL processes (and from different precursors under MTL conditions) are different does not necessarily imply that the surface ethyl groups are themselves different in structure. The ethanes derived from (COD)PtEt₂ are generated from a surface in which the predominant surface species are C₂ moieties and probably a mixture of C₈ moieties of different degrees of unsaturation; the ethanes from ethylene are from a surface on which only C₂ moieties are present. We speculate that the C₈ groups act as a source of hydrogen that serves to increase the local concentration of H(D)* near Et* moieties, and thus to increase the rate of reductive elimination as ethane relative to that when only C₂ groups are present on the surface.⁴² A fast rate of reductive elimination from the surface allows little time for exchange of H/D with the surface (eq 15). Thus, a faster rate of reductive elimination for Et* species derived from (COD)PtEt₂ than for those derived from ethylene rationalizes the lesser content of deuterium in the ethanes from (COD)PtEt₂ than those from ethylene.

(42) We have recently obtained additional data that support this hypothesis: under MTL conditions, the reduction in EtOD of a (DO)PtEt₂ complex (where DO is a diolefin that does not readily donate hydrogens to the surface of platinum) produces ethanes containing ca. 2.7 D. Complete details of this study will be reported separately.

(38) These results are consistent with those obtained from the reductions under RRL conditions of these substrates by D₂ in *n*-heptane.⁴ Previously, we argued that this difference in incorporation of deuterium (together with data from ²H NMR spectroscopy that located the position of the excess deuterium (i.e., $d_{av} > 1.00$) in the propanes) suggests that the exchange of hydrogens β to the surface of platinum is faster for secondary surface alkyls than for primary surface alkyls. The data presented here are also consistent with this interpretation.

(39) The data in Figure 8 show that the isotopic distributions of the propanes- d_n broaden with the following order of substrates: propylene < (COD)Pt(*n*-Pr)₂ < (COD)Pt(*i*-Pr)₂. In EtOD, the reductions of (COD)Pt(*n*-Pr)₂ and of (COD)Pt(*i*-Pr)₂ by D₂ produced distributions of propanes- d_n similar to those produced in *n*-heptane.⁴ The reductions of propylene, however, produced distributions of propanes- d_n that were narrower in EtOD than in *n*-heptane. We can rationalize this observation as follows: the rate of C–H bond activation of propyl* moieties (relative to the rate of reductive elimination as propanes- d_n) is slower (1) in ethyl alcohol than in *n*-heptane,⁴⁰ and (2) when cyclooctyl* moieties are coadsorbed than when they are absent.⁴¹ As a consequence, the isotopic distributions of the propanes- d_n from propylene sharpen in EtOD relative to *n*-heptane, and those distributions generated from the platinum complexes are not noticeably affected by the change of solvent.

(40) The data in Table III for reductions of (COD)Pt(CD₃)₂ support this argument. This result may be general for all surface alkyls on platinum. In a future paper, we will examine the influence of the solvent on the rate of C–H bond activation of surface alkyls.

(41) The data in Table IV for reductions under MTL conditions of ethylene and of (COD)PtEt₂ support this argument.

Analysis of the isotopic compositions of the cyclooctanes is complimentary. Under MTL conditions, the cyclooctanes produced from the reductions of (COD)PtEt₂ contained more deuterium (consistent with loss of hydrogen to Et*) than those produced from the reductions of COD (Table IV). We observed the same phenomenon under RRL conditions. The similar reactivities of cyclooctyl* moieties in both kinetic regimes indicate that the mechanism for reduction of (COD)PtEt₂ is probably the same in both regimes. The observation that coadsorbed Et* moieties are not affected by this additional contribution of H(D)* to the surface pool under RRL conditions suggests that the addition of H(D)* (via loss of H from cyclooctyl*) to a hydrogen-rich surface is not significant.

In broad terms, these isotopic experiments continue to support our hypothesis that heterogeneous hydrogenation of (COD)PtR₂ complexes generates platinum surface alkyls (R*) similar to those obtained by the hydrogenations of olefins. The environment in which the surface alkyls from (COD)PtR₂ are generated is, however, clearly different, at least under MTL conditions, from that experienced by the surface alkyls generated by simple hydrogenations of olefins.

Mechanism of Reaction. Specifying the mechanism of most heterogeneous reactions is difficult because a number of processes are usually occurring simultaneously on the surface. We have enough information about the heterogeneous hydrogenations of (COD)PtR₂ complexes to be able to specify important classes of reactions and steps, but usually not enough to be able to specify detailed rates or structures of all intermediates. We comment on the individual steps.

(i) (COD)PtR₂ + Pt(O) → [(COD)Pt*R₂] → COD* + 2R*. The evidence that the (COD)PtR₂ complexes must adsorb on the surface of the catalyst for reaction to occur is now firm. We presume that initial adsorption occurs at platinum, because it is the most polarizable part of the molecule. This presumption is supported by stereochemical evidence.^{4,5} We believe that these steps are irreversible: no deuterium is incorporated into (COD)PtR₂ complexes in solution.⁴

(ii) H₂ + Pt(O) → 2H*. The chemisorption of H₂ in this reaction is probably very similar to that in other hydrogenations. It is usually only weakly competitive with olefins^{21,22} (and we expect with (COD)PtR₂ complexes) for vacant sites on the surface of the catalyst.

(iii) H* + ROD ⇌ D* + ROH. The facility of this exchange is a key to using this reaction mechanistically. The exact mechanism of the exchange has not been established, but the rate of exchange is only dependent on acidity at very high pH. A previous paper contains additional evidence concerning this reaction.⁷

(iv) (C₈H_n)* ⇌ (C₈H_{n-1})* + H*; (RH_n)* ⇌ (RH_{n-1})* + H*. The reversible exchange of H/D between the surface alkyls and the surface of the catalyst can be faster than reductive elimination of alkane. The rate of this process is dependent on the structure of the surface alkyl and on the reaction conditions: exchange of cyclooctyl* moieties is fast while that of R* moieties is slow; exchange under MTL conditions is fast while that under RRL conditions is slow. Qualitatively, it seems that most (if not all) of the H* lost by the alkyl groups exchanges into the protic solvent before adding to another R* or C₈* group. Nevertheless, there is still probably a flux of H/D (defined strictly as H or D by exchange with EtOH or EtOD) between coadsorbed surface alkyls.

(v) R* + H* → RH. The final reductive elimination of alkanes is important and possibly the overall rate-limiting step. Different alkyl groups will doubtless eliminate at different rates. We believe that release of methane or ethane on hydrogenation of (COD)PtR₂ (R = CH₃ or C₂H₅) is faster than the release of cyclooctane. Our results are consistent with a mechanism for the reduction of (COD)PtEt₂ in which the Et* moieties are reduced, in part, by H(D)* generated by C-H bond activation of the coadsorbed cyclooctyl* moieties that, as a result of this loss of H(D)*, become more dehydrogenated than cyclooctyl* moieties derived from COD; the resulting cyclooctanes therefore contain more deuterium than those produced from COD.^{42,43}

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(43) It is possible that the higher content of deuterium in the cyclooctanes produced from the platinum complexes than those produced from COD results from the incorporation of deuterium into the cyclooctyl moieties of adsorbed intact platinum complexes. No deuterium is found, however, in (COD)PtMe₂ reisolated from reductions by D₂ in *n*-heptane.⁴ This result argues against the incorporation of deuterium into adsorbed intact platinum complexes since the mechanism of reduction proceeds by *initial* adsorption of the platinum atoms in the complexes. It is difficult for us to believe that C-H bond activation of the COD in (COD)PtR₂ takes place *after* irreversible adsorption, but *before* irreversible dissociation.