Reports

Catalytic Hydration of Terminal Alkenes to Primary Alcohols

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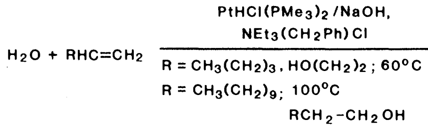
Direct catalytic hydration of terminal alkenes to primary alcohols would be an inexpensive route to industrially useful alcohols and a convenient synthetic route for the synthesis of terminal alcohols in general. The reaction between *trans*-$PtHCl(PMe_3)_2$ (where Me = CH_3) and sodium hydroxide in a one-to-one mixture of water and 1-hexene yields a species that, at 60°C and in the presence of the phase-transfer catalyst benzyltriethylammonium chloride, catalyzes selective hydration of 1-hexene to *n*-hexanol at a rate of 6.9 ± 0.2 turnovers per hour. Hydration of 1-dodecene to *n*-dodecanol occurs at a rate of 8.3 ± 0.4 turnovers per hour at 100°C. Deuterium labeling experiments with *trans*-$PtDCl(PMe_3)_2$ show that hydration involves reductive elimination of a C–H bond. At low hydroxide concentrations (<8 equivalents), hydration of the water-soluble olefin 3-butene-1-ol to 1,4-butanediol exhibited a first-order dependence on hydroxide concentration for loss of catalytic activity. This suggests that hydroxide attacks the coordinated alkene slowly. At high hydroxide concentrations, the rate of catalysis was hydroxide-independent and first-order in alkene. Substitution of coordinated water ($k_1 = 9.3 \pm 0.5 \times 10^{-3}$ liters per mol per second) appears to be limiting under these conditions.

Direct hydration of alkenes is a commercial process for the synthesis of alcohols (*1*). Catalysts for this transformation include phosphoric acid (*2*), transition metal oxides (*2, 3*), zeolites (*4*), and clays (*5*). These catalysts require moderate to high operating temperatures and pressures. They are of limited use because addition of water obeys Markovnikov's rule and primary alcohols are not obtained. Although anti-Markovnikov hydration can be effected by stoichiometric reactions, such as hydroboration, catalytic processes for this transformation are lacking.

Straight-chain primary alcohols are used widely in surfactants, plasticizers, and detergent precursors. Methods for their synthesis include copper oxide– or chromium oxide–catalyzed hydrogenolysis of fats and oils and hydrolysis of oxidized trialkylaluminums produced by the growth reaction (*2*). Both methods require high pressures and temperatures. Alternatively, hydroformylation of terminal olefins followed by reduction of the aldehyde product provides an indirect route to terminal alcohols (*2*). Palladium-catalyzed telomerization of dienes to isomeric mixtures of dienols (*6*) is, to our knowledge, the sole example of direct catalytic hydration of alkenes to primary alcohols; however, low selectivity is observed. We now report the selective hydration of unactivated terminal alkenes to primary alcohols, catalyzed by *trans*-$PtH(OH_2)(PMe_3)_2^+$ under mild conditions, as well as mechanistic information about this reaction.

Reaction mixtures consisted of water (0.30 ml), alkene (0.50 ml), aqueous NaOH (1.0*M*, 0.20 ml), $PtHCl(PMe_3)_2$ [7.7 mg (0.02 mmol)], and $NEt_3(CH_2Ph)Cl$ [10.0 mg (0.05 mmol)], the latter acting as a surfactant (Me = CH_3, Et = C_2H_5, and Ph = C_6H_5). In a study (*7*) of catalytic hydration of nitriles to amides we showed that the first complex generated is [*trans*-$PtH(OH_2)(PMe_3)_2$]OH. Alternatively, [*trans*-$PtH(OH_2)$ $(PMe_3)_2$]PF_6 (*7, 8*) can be used directly as a catalyst (with 1 equivalent of NaOH); however, the preparation of *trans*-$PtHCl(PMe_3)_2$ is most convenient (*9*). The sensitivity of these systems to air required use of thoroughly deoxygenated water and alkenes. The mixtures were stirred in sealed ampoules, which were heated in a constant-temperature bath. At 60°C selective hydration of 1-hexene to *n*-hexanol occurred at a rate of 6.9 ± 0.2 turnovers per hour (error limits are standard errors of the reported values for seven determinations), whereas at 100°C 1-dodecene was converted to *n*-dodecanol at 8.3 ± 0.4 turnovers per hour (for three determinations) (Eq. 1). Only traces of branched alcohols (<0.5%) were detected in the product mixture by gas chromatographic analysis. Products were identified by comparison of their proton nuclear magnetic resonance (NMR) spectra (300 MHz) with those of samples of the 1- and 2-substituted alcohols. Control reactions, without $PtHCl(PMe_3)_2$, without NaOH, or without $[NEt_3(CH_2Ph)]Cl$ showed no catalytic activity. Reaction mixtures were analyzed by gas chromatography. The organic phases were found to contain >96% of the alcohol produced (*10*).



$$H_2O + RHC{=}CH_2 \xrightarrow[\substack{R = CH_3(CH_2)_3,\ HO(CH_2)_2;\ 60^\circ C \\ R = CH_3(CH_2)_9;\ 100^\circ C}]{\substack{PtHCl(PMe_3)_2/NaOH, \\ NEt_3(CH_2Ph)Cl}} RCH_2{-}CH_2OH \qquad (1)$$

The two phases of an active catalytic mixture were separated and used to reconstitute two catalytic mixtures. Only the aqueous phase retained catalytic activity. From ^{31}P NMR spectra the metal complex could be detected only in the aqueous phase. To eliminate the possibility that a spectroscopically insignificant amount of highly active catalyst was formed, by partitioning of platinum species into the organic layer, we performed a dilution experiment. Increasing the volume of water should decrease the amount of catalyst present in the organic layer if an equilibrium partitioning of platinum species occurs between the layers. When the volume of the aqueous phase was increased threefold (under conditions where the rate was hydroxide-independent), there was no decrease in net alcohol production. Conversely, if the volume of the hexene layer was doubled or tripled while keeping the aqueous phase constant, there was no increase in the net alcohol production. Therefore, most catalysis occurs in the aqueous layer.

A deuterium labeling experiment with *trans*-$PtDCl(PMe_3)_2$ used as the catalyst precursor for hydrolysis of 1-hexene showed incorporation of label into the β C–H bond of the alcohol product (*11*). The reaction mixture was analyzed by ^2H NMR spectroscopy at 30.71 MHz. No deuterium label was detected in the aqueous phase. The spectrum of the organic phase contained a signal at 1.25 ppm [relative to benzene-d_6 (perdeuterated benzene) at 7.14 ppm]. Thus, deuterium incorporates into the β position of *n*-hexanol. This result suggests that catalytic hydration requires a C–H reductive elimination step and occurs by the mechanism proposed in Fig. 1. Another mechanism consistent with the labeling study involves migration of hydride to the olefin, forming an *n*-alkyl ligand, followed by nucleophilic attack at platinum by hydroxide and reductive elimination to yield a

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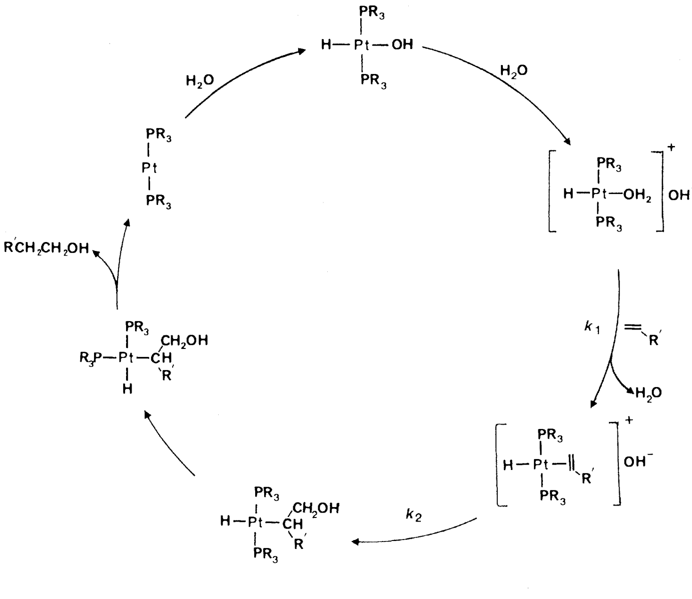

Fig. 1. Proposed catalytic cycle for the hydration of terminal olefins to primary alcohols.

terminal alcohol. This alternative seems unlikely because similar alkyl-hydroxo complexes of platinum are stable (*12, 13*), however, the phosphine ligands used were bulkier.

We circumvented kinetic complications introduced by a two-phase system by examining hydration of 3-butene-1-ol, a water-soluble alkene, to 1,4-butanediol. Cyclization to tetrahydrofuran was not observed under the mildly basic conditions of catalysis. At low alkene concentrations (<10% by volume) hydration occurs without formation of alcoholysis by-products. Below $[OH^-] = 2 \times 10^{-1}M$, the rate of hydration of 3-butene-1-ol (Fig. 2) shows a first-order dependence on $[OH^-]$ for catalyst stability. Initial rates are unchanged. We attribute the remarkable selectivity for anti-Markovnikov addition to steric control of hydroxide addition to the complexed olefin. More hindered olefins such as *cis*- and *trans*-3-hexene are not hydrated, and the analogous catalyst system with PEt_3 as the ligand does not show activity under the conditions described here.

The catalyst stability and rate of olefin hydration is independent of $[OH^-]$ as its concentration increases (Fig. 2). At elevated $[OH^-]$, the rate law is first-order in the alkene concentration. This allows the determination of $k_1 = 9.3 \pm 0.5 \times 10^{-3}M^{-1}$ sec^{-1} (the rate of displacement of coordinated water by 3-butene-1-ol). The k_1 step can be observed spectroscopically by both ^1H and ^{31}P NMR. Treatment of a solution of *trans*-$[PtH(H_2O)(PMe_3)_2][PF_6]$ (*14*) with 5 equivalents of 1-hexene results in irreversible quantitative formation of *trans*-$[PtH(CH_2 = CH(CH_2)_3CH_3)(PMe_3)_2][PF_6]$ (*13, 15*). Similar substitution of *trans*-$[PtH(H_2O)(PEt_3)_2][PF_6]$ by 2-butyne occurs at −30°C (*8*).

The catalyst system described here has several novel features. Unlike the palladium(II)-catalyzed Wacker process, oxidation to aldehyde products is not observed. Presumably the small PMe_3 ligand allows rapid *cis-trans* isomerization and reductive elimination of alcohol product before β elimination to aldehyde occurs. As noted above, insertion of coordinated olefin into the Pt–H bond does not interfere with catalysis. The anti-Markovnikov mode of addition may be sterically controlled; however, when palladium(II)-olefin complexes undergo attack by external nucleophiles, normal Markovnikov addition usually holds (*16*). Possibly the sterically unhindered platinum system can bind hydroxide before it adds to the coordinated olefin. There is precedent (*16, 17*) that this mode of addition leads to anti-Markovnikov products. This research establishes the feasibility of direct catalytic hydration of terminal alkenes to primary alcohols, an important class of chemicals.

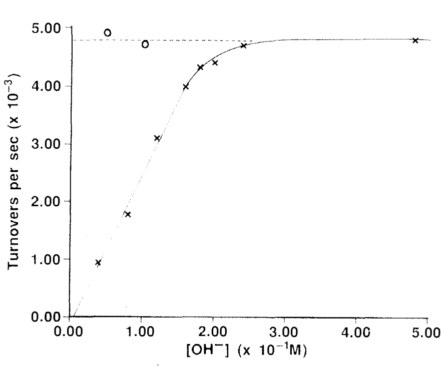

Fig. 2. Dependence of the rate of $[PtH(H_2O)(PMe_3)_2][OH]$–catalyzed hydration of 3-butene-1-ol on the hydroxide concentration at 60°C. The points marked x were for rates determined at 3-hour analysis times. Those marked with o are extrapolated intitial rates.

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13. Furthermore, the ^1H NMR spectrum of an acetone-d_6 solution of $[PtH(H_2C = CH(CH_2)_3CH_3)(PMe_3)_2][PF_6]$, after standing for 45 minutes at 25°C, shows a significant decrease in the intensity of the hydride and vinyl resonances. This suggests slow insertion of coordinated alkene into the metal hydride bond [see H. C. Clark and H. Kurosawa, *Inorg. Chem.* **11**, 1275 (1972)]. Because of the reversibility of this reaction (*8*) as well as the rapidity of nucleophilic attack by hydroxide on coordinated alkene, this reaction does not represent a major competing pathway to the catalytic sequence.
14. The complex was prepared by addition of water to an acetone-d_6 solution of $[PtH(acetone)(PMe_3)_2]$ $[PF_6]$. ^{31}P $\{^1H\}$ NMR (80.99 MHz) [$\{^1H\}$ denotes broadband proton decoupled, δ denotes the chemical shift in parts per million upfield from 85% H_3PO_4 for ^{31}P NMR or from tetramethyl silane for ^1H NMR spectra, and *J* denotes the coupling constant]: $\delta = -18.7$ ppm, $J_{Pt-P} = 2811$ Hz. ^1H NMR (360.247 MHz) δ ppm: −25.4 $J_{Pt-H} = 1421$ Hz, $J_{P-H} = 14$ Hz (Pt–H); 1.2 $J_{Pt-H} = 33$ Hz, $J_{P-H} = 7$ Hz ($P-CH_3$).
15. ^{31}P $\{^1H\}$ NMR (80.99 MHz): $\delta = -8.2$ ppm, $J_{Pt-P} = 2183$ Hz. ^1H NMR (360.247 MHz) δ ppm: −8.73 $J_{Pt-H} = 1024$ Hz, $J_{P-H} = 14$ Hz (Pt–H); 3.23 m (multiplet) ($Pt\text{-}H_2C = C\mathit{H}R$); 4.35 m ($Pt\mathit{H}_2C = C\mathit{H}R$) (italics identify the resonances being measured). The methyl resonances of the PMe_3 groups were not observed because of interference from signals of the methylene protons of 1-hexene.

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Coastal Uplift and Mortality of Intertidal Organisms Caused by the September 1985 Mexico Earthquakes

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Coastal uplift associated with the great Mexican earthquake of 19 September 1985 and its principal aftershock produced widespread mortality of intertidal organisms along the coast of the states of Michoacán and Guerrero, Mexico. Measurements of the vertical extent of mortality at ten sites provided estimates of the magnitude of the vertical component of deformation along the coast. Within the affected area, uplift ranged from about 12 centimeters to about 1 meter, and no subsidence was observed. The observations are consistent with models of the tectonic deformation that results from buried slip on a shallow-dipping underthrust fault.

THE MEXICAN EARTHQUAKES OF 19 and 21 September 1985 (surface wave magnitudes 8.1 and 7.5, respectively) ruptured a portion of the northeastward dipping thrust fault lying between the Cocos Plate and the North American Plate under Mexico. Preliminary aftershock locations indicated that the combined rupture zone was about 240 km long and 70 km wide, was elongated parallel to the trench axis but was landward of the trench, and was below the shoreline of the coasts of Michoacán and Guerrero, Mexico (*1*) (Fig. 1). The vertical component of tectonic deformation associated with the rupture produced a static offset in land level relative to mean sea level.

In the absence of sea level gauges in the rupture area, we surveyed the vertical distribution of intertidal organisms to document local deformation (*2*). Zonation of intertidal species is determined by biotic and abiotic factors that are ultimately related to tidal cycles (*3, 4*). In the high intertidal zone, duration of emergence may determine the upper limit of a sessile species' range because of desiccation and temperature stress. Significant uplift will therefore induce mortality among sessile species whose upper limits are determined by duration of emergence at low tide. Subsidence will introduce previously supralittoral substratum into the littoral zone, where it will be rapidly colonized by algae. The extent of either the resultant mortality or colonization will reflect the magnitude of the local vertical component of tectonic deformation. Darwin (*5*) used such evidence to infer uplift caused by the Chilean earthquake of 1835, and other investigators (*6*) have done so more recently.

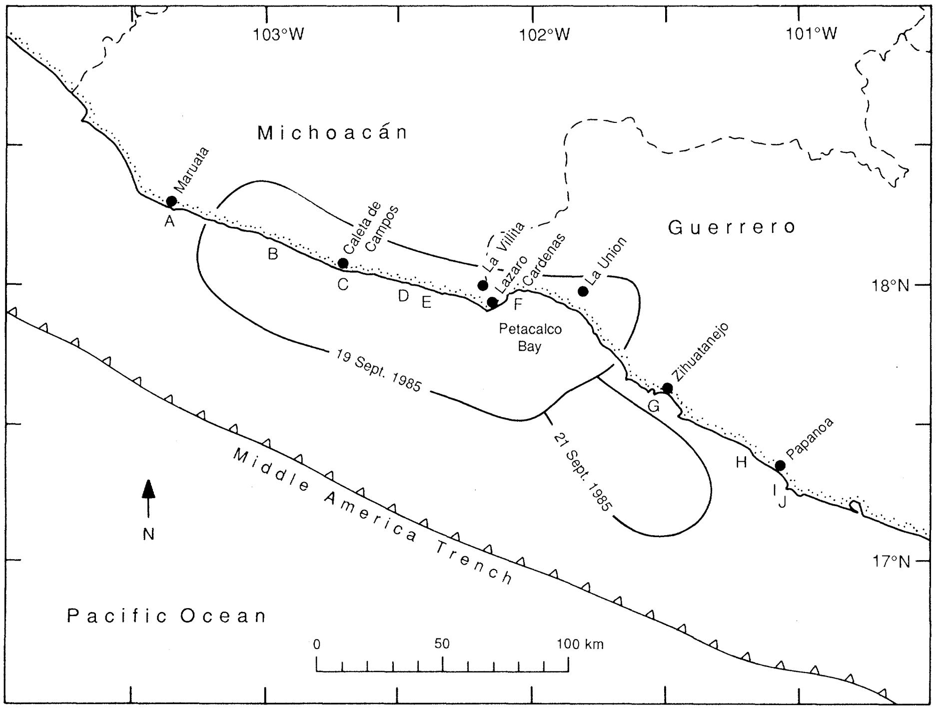

Fig. 1. The coast of the states of Michoacán and northern Guerrero, Mexico. The preliminary aftershock zones of the earthquakes of 19 and 21 September 1985, are outlined (*1*). Sites at which the intertidal organisms were surveyed are indicated by the letters A through J. The Cocos Plate forms the floor of the Pacific Ocean southwest of the Middle America Trench and is being thrust northeast under the North American Plate at the trench axis. The depth of the fault beneath the shoreline is about 20 to 25 kilometers (*1*).

A 6-day survey indicated that uplift had caused mortality among intertidal organisms, and evidence of this was widespread throughout the epicentral region. Uplift-induced mortality was most obvious among macroalgae, both because algae were dominant space-holders in the intertidal and mortality was not always readily apparent in shelled invertebrates. Coralline algae were particularly good indicators of mortality because they discolored rapidly after death (*7*). The preearthquake vertical range of some algal species exceeded the magnitude of uplift; thus both living and dead specimens could be found at each site. The vertical distance between these uppermost living and dead specimens was measured for certain species at ten sites (Fig. 1, A–J) (*8*). This measurement gives an estimate of the vertical extent of mortality (VEM), and represents the difference in a species' upper intertidal limit before and after uplift.

Measurements of the algal mortality that resulted from coastal uplift associated with the earthquakes are shown in Table 1. The northernmost site, Maruata, showed no large-scale mortality and is therefore considered to lie beyond the uplifted zone. Farther south, there was evidence of widespread mortality among both the crustose corallines (Fig. 2a) and the articulated corallines (Fig. 2b), as well as among species of *Gracilaria, Ralfsia, Padina, Chaetomorpha*, and *Cladophora*. The VEM exceeded 60 cm at Caleta de Campos (site C) and decreased north and south of this site. The VEM was smallest at the southern sites (sites F–J), where most values were less than 25 cm. We were unable to determine the southern boundary of the

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