

Intramolecular 1-3 Hydrogen Shifts During Hydrogenation of C=C Double Bonds over Noble Metal Catalysts

Gerard V. Smith^{a,b,c}, Boris Rihter^b, Mihály Bartók^d, Ágnes Zsigmond^{c,d}, and Ferenc Notheisz^{c,d}

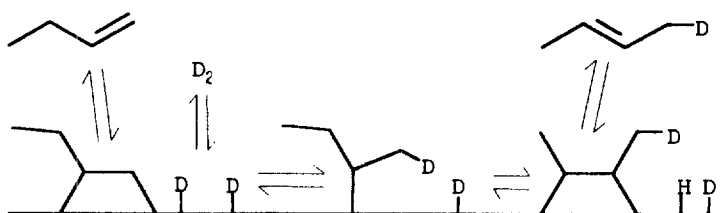
^aDepartment of Chemical Engineering, Center for Catalytic Technology, Pohang University of Science and Technology, Pohang, Korea; ^bDepartment of Chemistry and Biochemistry, ^cMolecular Science Program, Southern Illinois University, Carbondale IL 62901, United States of America; ^dDepartment of Organic Chemistry, József Attila University, Dóm tér 8, 6720 Szeged, Hungary

Introduction

Hydrogenation and isomerization of alkenes can usually be described by the Horiuti-Polányi mechanism¹. In fact, this mechanism is so successful at describing the events occurring during hydrogenation that it is now referred to as the classical mechanism of hydrogenation.

During hydrogenation with deuterium (deuteriumation), this classical mechanism predicts that double bond migration will put deuterium into the allylic position.

Horiuti-Polányi (classical) mechanism for double bond migration.

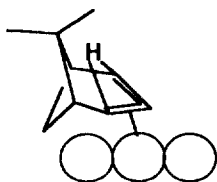


Although this mechanism appears straight forward and unambiguous, some disturbing results have been reported over the years which are not readily explained by this classical mechanism. For example, in certain instances during deuteriumations the double bond shifts but deuterium is not incorporated into the allylic position.

Thus, early deuteriumations with (+)-apopinene² showed that isomerized apopinenes contain very little deuterium and that isomerization is much faster than deuterium incorporation into the allylic position. Therefore it seemed probable that isomerization takes place through an intramolecular hydrogen shift which preserves the endemic hydrogen within the isomerizing apopinene. To account for this result, a sigmatropic 1,3-hydrogen shift was suggested, in which the allylic *endo*-H shifted (*this is a top shift of the*

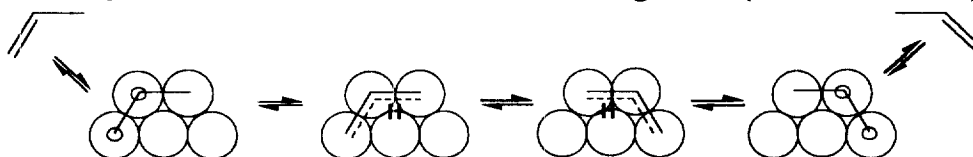
hydrogen)³. Such a topside shift would also account for the apparent *trans* addition of hydrogen occurring during certain hydrogenations⁴.

1,3-top side hydrogen shift



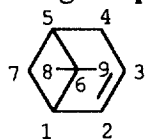
Although theoretical calculations originally showed this type of reaction to be symmetry forbidden in an unadsorbed molecule, calculations showed that it is allowed in a molecule adsorbed on transition metals^{5,6,7}. However, later theoretical calculations reversed this earlier calculation and suggested a 1,3-hydrogen shift in which the allylic *exo*-hydrogen is abstracted by the surface from an adsorbed alkene (either 1,2-diadsorbed or π -complexed) and the resulting π -allyl species moves over the abstracted hydrogen such that it adds to the former vinylic position and accomplishes a stepwise intramolecular 1,3-hydrogen shift (*this a bottom shift of the hydrogen*)⁸.

π -allyl shift mechanism for double bond migration (the bottom shift)



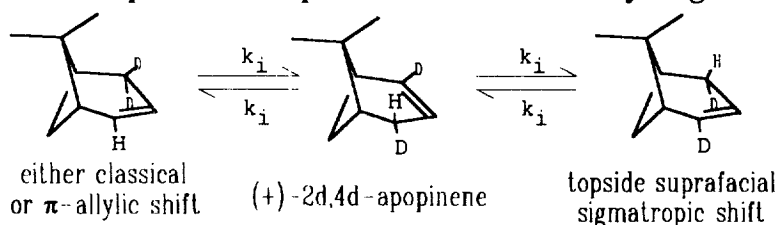
To distinguish between these two hydrogen shift mechanisms, (1*S*)-(-)-*exo*-2,4-dideuteroapopinene was constructed as a probe molecule. In this molecule a *top* shift of the allylic *endo*-H will not affect the deuterium content of the molecule, but a *bottom* shift of the allylic *exo*-D will decrease deuterium in the vinylic position (C2) and increase deuterium in the allylic position (C4).

Numbering in apopinenes



(-)-apopinene

Comparison of topside and bottom side hydrogen shifts



Experimental

By a ten-step route from α -pinene⁹, (1*S*)-(-)-*exo*-2,4-dideutero-apopinene was synthesized thrice with different deuterium concentrations. The hydrogen contents (19%, 15.1%, and 6.1%) of the molecules at the C2 position were determined by 200 MHz proton NMR with the C3 proton used as an internal standard.

Double bond migration (racemization) within (1*S*)-(-)-*exo*-2,4-dideutero-apopinene was studied on Pd-black, 0.46% Pd/SiO₂, 1.17% Pd/SiO₂, 0.4% Pd/Al₂O₃, 1.0% Pd/Al₂O₃, and Pd₈₀Si₂₀ metallic glass catalysts in both deuterium and hydrogen. Hydrogenations were run on neat apopinene (except where noted) in the liquid phase at one atmosphere of hydrogen or deuterium and were stopped at different percentages to furnish several different percentages of racemization. In the recovered alkenes from these reactions, the hydrogen contents at C2 were determined. The apparatus and the methods for studying the hydrogenation and for measuring percent dispersion (%D) of the catalysts by hydrogen chemisorption have been described earlier¹⁰.

Results and Discussion

Essentially, the same results are found for reactions in deuterium and hydrogen (Table 1). As double bond migration (racemization) proceeds, hydrogen content at C2 increases.

Table 1. Racemization of (1*S*)-(-)-*exo*-2,4-dideuteroapopinene on Pd catalysts in deuterium

| catalyst | racemization, % | % H content in C2 | |
|--|--------------------|-------------------|---------------------------|
| | | original % | final % |
| 0.46% Pd/SiO ₂ (60.5%D) | 38.9 | 19 | 36.3 |
| | 81.1 | 19 | 50 |
| | 48.9 | 19 | 38.6 |
| | 56.7 | 19 | 41.4 (in H ₂) |
| Pd ₈₀ Si ₂₀ metallic glass | 10.6 | 19 | 11.6 (in H ₂) |
| 1% Pd/Al ₂ O ₃ (49.0%D) | 30.8 | 19 | 31.9 |
| 0.4% Pd/Al ₂ O ₃ (77.5%D) [#] | 10.1 | 19 | 22.6 |
| Pd ₈₀ -Si ₂₀ metallic glass | 32.2 | 15.1 | 33.5 |
| | 39.6 | 15.1 | 34.4 |
| 1.17% Pd/SiO ₂ (40%D) [@] | 33.0 | 15.1 | 27.2 |
| Pd ₈₀ Si ₂₀ metallic glass | 62.9 | 6.1 | 35.5 |
| 0.46% Pd/SiO ₂ (60.5%D) | 68.0 | 6.1 | 36.1 |
| Pd-black | 57.3 | 6.1 | 32.3 |

[#] poisoned with carbon tetrachloride
[@] poisoned with carbon disulfide

Although the experiments are imperfect because the percentages of hydrogen at C4 are not known, little evidence exists for a 1,3-top shift. With the exception of the Pd₈₀Si₂₀ metallic glass experiment in hydrogen (fifth experiment from top in Table 1), all data fall near the lines calculated for a 1,3-bottom shift for the respective original percentages of hydrogen at C2. Therefore, it appears that the C4 allylic deuterium facing the catalyst shifts and that it is not readily diluted by incursion from other surface hydrogens or deuteriums. Either it shifts in a concerted fashion or it moves as proposed in the Anderson calculations⁹.

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