The Extent of Incorporation of Excess Deuterium in the Platinum-Catalyzed Reduction of Unsubstituted Cycloolefins by H₂ in D₂O/THF Increases with the Strain Energy of the Product Cycloalkanes

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Received August 9, 1990

This paper describes the isotopic compositions of cycloalkanes produced by the catalytic reduction of cycloolefins (C₆H₄=CH₂) using H₂ and platinum black in 1:1 v/v THF/D₂O (pD₂O = 1) (eq 1). We conducted the reductions under conditions in which the rate of mass transport of H₂ to the surface of the catalyst limited the rate of reaction. Under these conditions, H₂ on the surface equilibrates essentially completely with D₂O in solution. Figure 1 summarizes the isotopic compositions of the cycloalkanes. The important observations are as follows: (1) the isotope of hydrogen found in the cycloalkanes was predominantly that present in D₂O rather than that present in H₂; (2) the cycloalkanes contained deuterium in large excess of that required for stoichiometric

(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) We chose D₂O/THF (1:1 v/v; pD₂O = 1) because a survey of solvent systems indicated that this system yielded cycloolefins having the highest content of deuterium in reductions of cyclooctene.

(3) We performed the reductions in a specially designed round-bottomed flask (volume = 225 mL); a small test (volume ca. 10 mL) protruded from the bottom of the flask; a Swagelok valve and a rubber septum capped the flask. After charging the test with a stir bar (3/8 × 3/16 in.) and 40 mg of Pt black, we purged the test with Ar and added 0.5 mL of dry THF and 0.5 mL of D₂O (adjusted to pD = 1 with D₂SO₄). The apparatus was purged with a mixture of 10% H₂ in Ar for 1 min with stirring; the rate of rotation of the stir bar was 1400 rpm. We pressurized the vessel to 10 psi (pH₂ = 0.17 atm), stirred for 4 min, placed the flask in an oil bath (75 ± 3 °C), and stirred for 5 min. We removed the solvent via cannula and added the substrate (15-20 mg in 3 mL of D₂O/THF) via syringe. Stirring was started and continued for 1 h. Analysis by GC/MS indicated that all reductions were complete.


(5) Isotopic compositions were determined by GC/MS. The average content of deuterium, dₐ, describes the extent of incorporation of deuterium. Isotopic abundances were corrected for natural abundance of ¹³C. Values of dₐ are probably accurate to ±0.3 D.

\[ d_a = \frac{100}{N} \times \text{n(alkane-dₘ)} \]


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**Figure 1.** Isotopic distributions and values of dₐ, for the cycloalkanes from the reductions of the corresponding cycloolefins by H₂ and D₂O/THF (1:1 v/v; pD₂O = 1) over platinum black. The difference in values of dₐ from duplicate runs was, in all cases, ±0.2.

**Figure 2.** Values of dₐ/dₘ vs strain energies of cycloalkanes (C₆H₄=CH₂). For consistency, the strain energies are all calculated values, obtained using Macromodel V2.0.14,19 The line drawn through the points was determined by linear regression.
reduction of the double bond (approaching complete exchange of D for H in some cases); and (3) each substrate gave the per-deuterated isopomer as the major product.

The observation that extensively polydeuterated cycloalkanes can be produced from cycloolefins with H₂ as the reductant is remarkable and potentially useful in the synthesis of isotopically labeled compounds. The ability to incorporate deuterium into organic compounds by the metal-catalyzed reduction of olefins with H₂ and D₂O/THF avoids the need for D₂. In addition, this technique should be applicable to the incorporation of tritium into organic compounds.

Previous studies of the hydrogenation of olefins in protic solvents showed that surface alkyls on platinum rapidly undergo isotopic exchange of hydrogen with H (D) and that the product alkanes contain the isotope from the solvent (ROH or ROD). Our results demonstrate that by working under mass-transport-limited conditions, isotopic exchange can be made more extensive than in these earlier reports. The exchange undoubtedly requires exchange between H (D) and the OH (OD) group of the solvent (eq 2). The mechanism of the exchange shown in eq 2 is not well established, although several mechanisms have been proposed.²⁰⁻¹⁶

\[
\text{H} + \text{ROD} \rightarrow \text{D} + \text{ROH}
\]  

(2)

Because the exchange of H/D between the surface of platinum and the protic solvent is, under the conditions used here, faster than the conversion of surface alkyls to alkanes, the content of deuterium in the product alkanes provides a valuable mechanistic tool: a measure of the rate of exchange (and thus of C-H bond activation) of the surface alkyls relative to the rate of their reductive elimination as alkanes. Comparison of the ratio \( d_{\text{ov}}/d_{\text{m}} \) from the reduction of a series of cycloalkanes demonstrates the utility of this approach (Figure 2). These data indicate that the rates of C-H activation (relative to the rates of reductive elimination) of surface cycloalkyls decrease from cyclohexyl to cycloheptyl.

The value of \( d_{\text{ov}}/d_{\text{m}} \) correlates with the strain energy of the product cycloalkanes \((r = 0.95)^{17-19}\). Thus, as the cycloalkane is varied from one having low strain energy to one having high strain energy, the transition state for reductive elimination increases in energy relative to that for isotopic exchange. The two simple limiting hypotheses rationalizing this inference are that strain is relieved in the transition state for isotopic exchange (C-H activation) or that strain is concentrated in the transition state for reductive elimination.²¹ We emphasize that \( \Delta G^* \) for reductive elimination by reaction of R* with H₂ is dominated by the free energy term describing generation of H* by a mass-transport-limited process. We therefore hypothesize that the correlation in Figure 2 reflects primarily structure-dependent differences in rates of C-H activation.

The heterogeneous polydeuteriation of hydrocarbons probably involves some combination of αα-activation, αβ-activation, and π-allyl formation.²² The differences in strain energies between the transition states leading to these intermediates and the transition states leading to the cycloalkane products should correlate with \( d_{\text{ov}}/d_{\text{m}} \). Calculating strain energies for the intermediates is, however, too complicated to be approached through realistic models of surface species.²³ To date, our efforts to obtain a correlation between the experimental values of \( d_{\text{ov}}/d_{\text{m}} \) and relative strain energies calculated for simple models of surface intermediates have not been successful.

Acknowledgment. We thank our colleagues John Burns and Watson Lees for assistance with the force field calculations.

³¹ There are several reports in the literature of correlations between the strain energy and the rates of reaction of functionalized cycloalkanes. For recent examples, see: Schneider, H. J.; Schmidt, G.; Thomas, F. J. Am. Chem. Soc. 1980, 102, 1424–1425. Schneider, H. J.; Schmidt, G.; Thomas, F. J. Am. Chem. Soc. 1983, 105, 3556–3563.


²³ The hydrocarbon species believed to exist on the surfaces of noble metal catalysts were summarized recently: Cogen, J. M.; Maier, W. F. J. Am. Chem. Soc. 1986, 108, 7752–7762 and ref 22 of this paper.