

Photoassistance in Homogeneous Catalysis: Direct Modification of Rates and Selectivity of Wilkinson's Catalyst

INTRODUCTION

$\text{RhCl}(\text{PPh}_3)_3$, Wilkinson's Catalyst (1), has been reported and characterized as being an efficient highly selective homogeneous hydrogenation catalyst (2). When dissolved in benzene it is brightly colored and changes from a light yellow to a deep yellow upon addition of hydrogen to form the active catalyst species. There are strong absorptions throughout the uv-visible region due primarily to electronic transitions involving the central metal atom, where the expansion of the coordination sphere is thought to provide the active site for catalytic olefin hydrogenation.

The use of $\text{RhCl}(\text{PPh}_3)_3$ as a hydrogenation catalyst in various unsaturated systems has been studied extensively (2, 3) and details of the thermal mechanism by which it catalyzes these reactions have been identified (4). Reports of parallel isomerization reactions in selected cases have also been published (5, 6). One mechanism postulated for such isomerization involves the dimer of Wilkinson's Catalyst, $\text{Rh}_2\text{Cl}_2(\text{PPh}_3)_4$ (6), which has been identified in small amounts in solutions of the monomer in the presence of H_2 (7). The only report to date of which we are aware on ultraviolet photolysis in $\text{RhCl}(\text{PPh}_3)_3$ catalyst systems showed a substantial increase over the thermal rate of hydrogenation of cyclooctene (8). Iridium complexes similar to Wilkinson's Catalyst have been more extensively studied under the influence of ultraviolet irradiation and a distinction between photoactive and photoinduced active catalytic species has been suggested (9).

Here, we report the initial results of a study intended to examine the use of pho-

toassistance as a kinetic and mechanistic probe for homogeneous catalysis. Catalytic hydrogenation of cyclohexene and 1-hexene with Wilkinson's Catalyst serves as our model system. The catalyst was selected because of its efficiency, selectivity, and availability. The thermal hydrogenation of cyclohexene with this catalyst has been studied extensively and serves as a test system for any substantial modification to the kinetics we are able to make.

EXPERIMENTAL

Wilkinson's Catalyst, obtained from Strem Chemicals, was used without further purification. The olefin reactants were distilled over Na; benzene solvent was distilled over Na-K amalgam and degassed prior to use. H_2 and N_2 gases were passed through Redox and molecular sieve columns to trap oxygen and water before introduction into the system.

The studies were carried out in a round-bottomed quartz vessel. Olefin and catalyst concentrations of 1.0 M and 10^{-3} to 10^{-4} M, respectively, were used and hydrogen at ambient temperature was maintained at a constant pressure of 1 atm over the reaction mixture. Introduction of the catalyst and olefin followed the procedure of Wilkinson (1) using a glass cup containing a weighed amount of catalyst. Effective stirring was promoted with an angled magnetic bar which turbulently broke the surface of the liquid (10). The light source was a 1000-W medium-pressure Hg-Xe lamp backed with a parabolic reflector. Products were withdrawn by syringe at controlled intervals, quenched at reduced temperature, and analyzed by gas chromatography. Based on several prior studies in this laboratory, the

thermal rate for these reactions in the absence of light is known to remain constant over the full course of the experiment.

RESULTS AND DISCUSSION

Figure 1a graphically illustrates the variation in the rate of production of cyclohexane during the hydrogenation of cyclohexene under sequential thermal and photochemical conditions. This rate is observed to be directly and immediately affected by photolysis with a rapid increase in rate following the start of illumination and a subsequent decrease below the initial thermal rate after photolysis. The initial thermal turnover rate was measured to be 13.1

min^{-1} , which compares favorably with published reports for the reaction. The enhancement factor for the reaction during irradiation was 1.7 giving a turnover rate of 22.3 min^{-1} . The postirradiation rate of 7.9 min^{-1} represents a significant decrease from the initial thermal rate. It has not yet been determined whether this results from irreversible photochemical destruction of the catalyst, however. These findings can be compared to the results in Ref. (8) for cyclooctene hydrogenation which indicate an enhancement factor of 2.5 during irradiation and a continuation of the accelerated rate for at least 1 h after terminating the ultraviolet light source.

The second reactant studied to verify the above observation was 1-hexene, a simple, unbranched olefin. Figure 1b illustrates a typical result from an experiment identical to that performed with cyclohexene. The initial thermal turnover rate observed in this case was 11.5 min^{-1} . It should be noted that studies with even smaller concentrations of catalyst in this apparatus have yielded turnover rates as high as 39 min^{-1} for 1-hexene hydrogenation without illumination.

The photoassisted region for the 1-hexene system shows the influence of light in the overall reaction process even more dramatically than it did for cyclohexene. Both the kinetics and the selectivity of the catalyst are modified. Immediately following exposure to the light source, a rapid increase in the rate of production of *n*-hexane is observed. After 4–5 min the rate becomes constant with an enhancement factor of 1.4 above the initial thermal rate. A second increase in rate is observed upon termination of irradiation, but this increase is rapidly depressed to a level at 70% of the initial thermal rate.

More important is our observation of the isomerization reaction to 2-hexene in the presence of light shown in the bottom of Fig. 1b. Isomerization is not observed prior to photolysis, although under thermal conditions trace amounts of the isomerization products appear after a sufficient period of

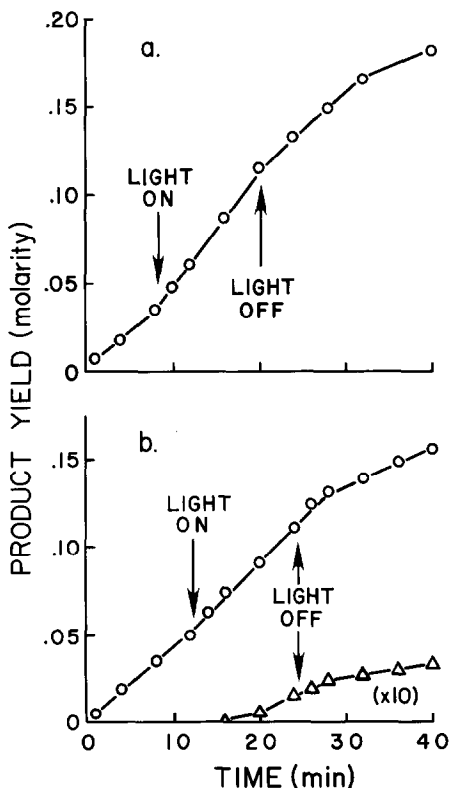


FIG. 1. (a) Product yield of cyclohexane during the thermal and photoassisted catalytic hydrogenation of cyclohexene with Wilkinson's Catalyst. Initial olefin and catalyst concentrations 1.0 and $3.3 \times 10^{-4} M$, respectively. (b) Product yields during the thermal and photoassisted catalytic hydrogenation and isomerization of 1-hexene with Wilkinson's Catalyst. Initial olefin and catalyst concentrations 1.0 and $3.6 \times 10^{-4} M$, respectively. *n*-hexane, \circ ; *cis*-2-hexene $\times 10$, \triangle .

time. These competing reactions also require the presence of catalyst and hydrogen. The concentrations of the *trans*-2 isomer observed during photolysis are 2 to 3 times greater than those of the *cis*-2 isomer, probably due in part to the latter's greater rate of hydrogenation (5). It should be noted that *isomerization continues after the light is removed* although at a somewhat slower rate.

Two additional comments regarding these results are appropriate. Thermal hydrogenation studies at elevated temperatures have shown our photoenhanced rates at 25° are equivalent to thermal rates at approximately 35°, and it is unlikely that the rapid response of the system to photolysis for hydrogenation is consistent with a purely thermal mechanism although some contribution to local heating cannot be ruled out. Finally, the decrease in postirradiation catalytic activity observed for thermal hydrogenation in these systems suggests that some of the catalyst is being degraded or converted to a new organometallic compound. Since 1-hexene undergoes isomerization at 25°C only during and after irradiation, it is possible that the new species generated is the active catalyst for the isomerization.

Additional experiments have demonstrated that the photoassisted, hydrogenation rate enhancement and the isomerization reactions are induced by light in separate spectral regions. A water-filled Pyrex filter was used to absorb both infrared radiation and ultraviolet light of wavelengths below 290 nm. Under these conditions, no photoenhancement of the hydrogenation rate was observed, although the initiation of isomerization was unperturbed. With the Pyrex filter in place the isomerization kinetics also showed a first-order dependence on light intensity. These results suggest that the change in selectivity of the catalyst derives from a new and substantially different mechanistic path for isomerization initiated photochemically with uv-visible light of wavelengths greater than 290 nm. Finally it is noted that the rate

of isomerization does show an inverse dependence on catalyst concentration which suggests that dimer formation is not responsible for this new catalytic process.

The characteristics of the experiments presented in this report are completely reproducible and we feel represent a general application of the use of light to energize the reactant state. This photoassistance of the catalytic process provides a new probe for the reaction coordinate which we are currently investigating for use in catalytic mechanism determination.

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J. R. PETERSON
D. W. BENNETT*
LEONARD D. SPICER

*Department of Chemistry
University of Utah
Salt Lake City, Utah 84112*

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* Current Address: Dept. of Chemistry and Geology, Clemson University, Clemson, South Carolina 29613