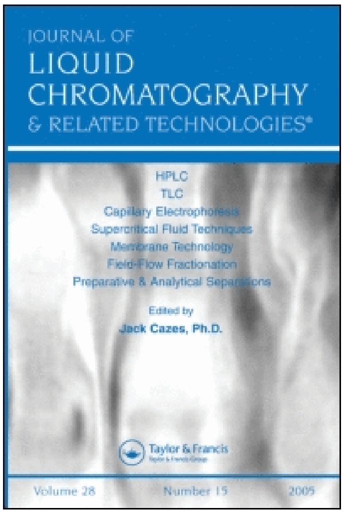

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HYDROGENATION KINETICS OF PHENYL PROPARGYL ETHER AS DETERMINED BY HIGH PRESSURE LIQUID CHROMATOGRAPHY*

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ABSTRACT

High pressure liquid chromatography (HPLC) was used to kinetically study the neat heterogeneous hydrogenation of an alkyne, phenyl propargyl ether. The study suggests that strong absorption of alkyne on the catalyst surface inhibits the further reduction of newly formed alkene to alkane.

INTRODUCTION

A literature survey revealed that high pressure liquid chromatography (HPLC) has not been recognized as a rapid, accurate and quantitative analytical method of resolving reaction products associated with the heterogeneous hydrogenation of alkynes, although acetylenes have been extensively studied in the gas phase (1,2), in solution (3,4) and more recently in the solid state (5,6). No liquid chromatography data was found discussing column/

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solvent systems in resolving individual alkynes, let alone resolving triple, double and single bonded species evolved during the neat hydrogenation of a parent alkyne. Since the neat hydrogenation of solid alkynes has found practical applications in solving problems associated with a hydrogen environment (7) a program was iniated to study the factors which influence the course of the catalytic reaction in the removal or control of hydrogen and its isotopes. The present study reports on the kinetics of the neat heterogeneous hydrogenation of phenyl propargyl ether using HPLC in lieu of more coventional techniques such as mass spectrometry and gas chromatography which could decompose or alter the reaction products.

METHOD

Apparatus

A Waters Associates Model ALC/GPC-502/401 dual detector liquid chromatograph equipped with a Model 6000A pump and a U6K closed loop injector was used in connection with two micro-Porosil columns (each 7 mm i.d. x 30 cm, Waters Associates). An isocratic solvent, 99% hexane and 1% methyl isobutyl ketone, was maintained at a rate of 0.4 ml min^{-1}. This column/solvent systems was chosen for use after conducting an extensive evaluation of resolving capabilities of many column/solvent combinations. These particular columns and flow rate yielded a column pressure of 460 psi (10^3 psi = 6.89 N mm^{-2}). The hydrogenation apparatus used in this study has been described by Courtney and Harrah (5).

Procedure

Hydrogenations were conducted by adding a weighed amount of palladium black (Fisher Scientific Company, Fair

Lawn, New Jersey) to the glass reaction container, followed by the additon of a weighed amount of phenyl propargyl ether (Farchan Research Laboratory, Willoughby, Ohio). The weighing vial and delivery funnel used to transfer the phenyl propargyl ether (PPE) to the reaction flask were rinsed three times using a total of about 20 ml of ethyl ether. After most of the ethyl ether had evaporated, the thick slurry was spread as uniformly as possible up to a prescribe mark on the glass vessel until evaporation of the ethyl ether was complete. The glass container was then placed inside the calorimeter bomb. After evacuation, the system was back-filled with hydrogen.

The initial hydrogen pressure varied from 100-500 mm Hg depending on the experiment. The hydrogen uptake (pressure drop) and any temperature change were monitored as a function of time. In certain experiments total hydrogen uptake was measured at reaction completion after 24 hours, while the kinetic experiments were stopped at various extents of hydrogenation by evacuating the residual hydrogen from the reaction container and back-filling with air.

In order to determine the point of complete coverage of the catalyst by alkyne, the total hydrogen uptake was determined for various PPE/Pd black ratios using a constant Pd black weight of 0.30 gm. The amounts of PPE used ranged from 0.20-1.00 gm. A stoichiometric uptake of hydrogen, based on the amount of PPE used, was achieved at a PPE/Pd black ratio of 1.66. This ratio of alkyne to catalyst was maintained in the kinetic experiments but the amount of catalyst used was reduced to 0.113 gm in order to complete all kinetic experiments with the same batch of catalyst.

The kinetic experiments were run by weighing 0.187 gm PPE and 0.113 gm Pd black, mixing and placing in the bomb reaction chamber as previously described, then evacuating and back-filling the reaction chamber to an initial hydrogen pressure of 100 mm Hg. The hydrogenation was allowed to proceed to a previously calculated pressure drop, i.e., extent of hydrogenation, then stopped by evacuating the residual hydrogen from the reaction container and back-filling with air. The contents of the glass vessel were rinsed with 28 mls of solvent, 99% hexane and 1% methyl isobutyl ketone (V/V), and the suspension filtered through a 0.45 μ Fluoropore membrane using a Waters' clarification kit assembly (Waters Associates, Milford, Massachusetts). The clear filtrate (10 ml) was then injected in the chromatograph. Both the refractive index detector and the 254 nm ultraviolet detector systems were used to monitor the chromatographic separation of the hydrogenation products, i.e., alkyne, alkene, alkane.

It was determined that the extinction coefficients of phenyl propargyl ether (PPE), allyl phenyl ether (Aldrich Chemical Company, Milwaukee, Wisconsin), and propyl phenyl ether are essentially equivalent at 254 nm and that there is a linear relationship between ultraviolet absorption at 254 nm and the amount of alkyne injected into the chromatograph. The relative concentrations of the hydrogenation products resolved by HPLC were determined by cutting out the ultraviolet peaks for the various components and weighing. The peaks were identified by injecting known samples of phenyl propargyl ether, allyl phenyl ether, and propyl phenyl ether and noting their elution volumes.

RESULTS AND DISCUSSION

In Figure 1 the dashed line denoting a stoichiometric uptake of hydrogen, based on the amount of PPE used, goes through the point representing a PPE/Pd black ratio of 1.66. For ratios less than or greater than 1.66 the uptake of hydrogen is less than stoichiometric. Therefore, the ratio of 1.66 is considered to be the point of complete coverage for the experimental technique employed. Since at the lower ratios not enough PPE was used to completely cover the Pd black surface, the thermal effects due to the hydrogenation reaction probably vaporized some of the PPE from the surface resulting in less than a stoichiometric amount of hydrogen being reacted. The amount of PPE vaporized from the

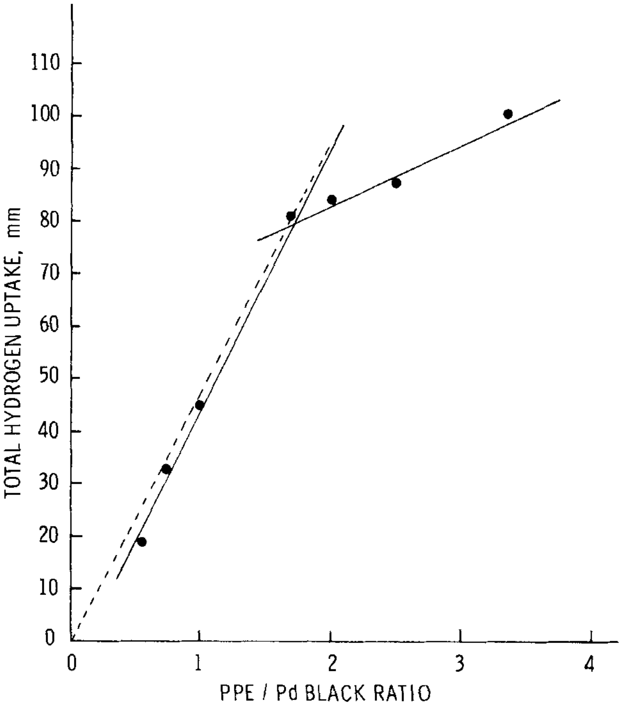

Figure 1. Total hydrogen uptake as a function of the PPE/Pd black ratio. The dashed line represents stoichiometric hydrogen uptake, while the solid lines represent experimental hydrogen uptake.

Pd black surface continually decreases until the ratio of 1.66 is reached, at which time the Pd black surface is completely covered and the uptake of hydrogen is stoichiometric. For ratios greater than 1.66 the reaction becomes controlled by diffusion of the liquid organic to the catalyst surface.

Figure 2 shows the type of data generated when this HPLC system was used to resolve the various species obtained on hydrogenation of phenyl propargyl ether. Figure 2 presents chromatograms at different extents of hydrogenation and shows that the more unsaturated a component is, the longer it is retained on the columns. The alkane (propyl phenyl ether) is eluted first,

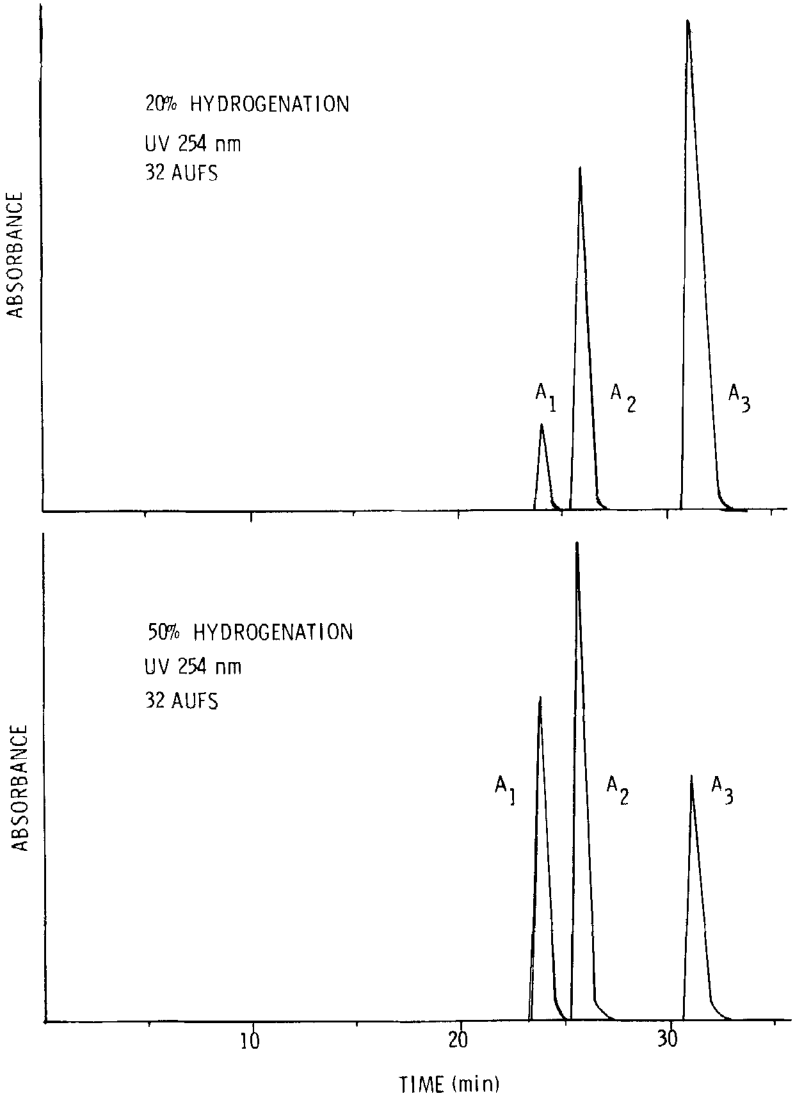

Figure 2. Chromatograms of phenyl propargyl ether at different extents of hydrogenation. A_1, A_2, and A_3 refer to the propyl phenyl ether, allyl phenyl ether, and propargel phenyl ether peaks respectively.

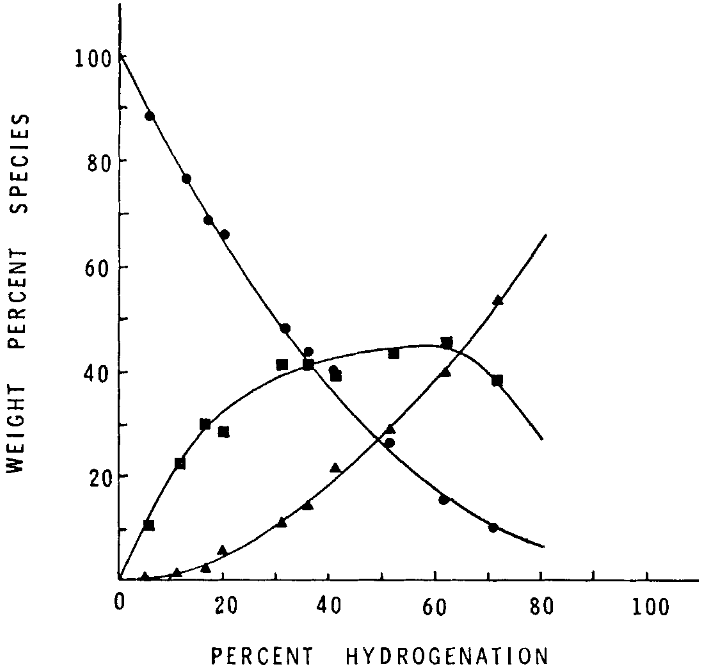

Figure 3. The weight per cent of species present at different extents of hydrogenation. Phenyl propargyl ether ●, allyl phenyl ether ▲, and propyl phenyl ether ■.

followed by the alkene (allyl phenyl ether), and finally the alkyne (phenyl propargyl ether).

The weight per unit of species present at different extents of hydrogenation can be readily generated from data such as that in Figure 2. Figure 3 presents this weight percent data as a function of percent hydrogenation of alkyne to alkane, i.e., phenyl propargyl ether to propyl phenyl ether. The following reactions and corresponding rate expressions can be written to describe the hydrogenation process presented in Figure 3:

$$A_3 + H_2 \xrightarrow{k_1} A_2 \qquad (1)$$

$$A_2 + H_2 \xrightarrow{k_2} A_1 \qquad (2)$$

where A_3, A_2 and A_1 represent phenyl propargyl ether (PPE), allyl phenyl ether, and propyl phenyl ether respectively. For the foregoing reactions, the rate equations are as follows:

$$\frac{d[A_3]}{dt} = - k_1[A_3](P_{H_2}/RT) \tag{3}$$

$$\frac{d[A_2]}{dt} = k_1[A_3](P_{H_2}/RT) - k_2[A_2](P_{H_2}/RT) \tag{4}$$

$$\frac{d[A_1]}{dt} = k_2[A_2](P_{H_2}/RT) \tag{5}$$

Equations 3 through 5 represent the rate of disappearance of triple bonds (A_3), double bonds (A_2), and the rate of formation of single bonds (A_1) respectively. The hydrogen concentration term was replaced by P_{H_2}/RT using the Ideal Gas Law. Thus, concentration may be expressed in terms of the total volume of the reaction vessel.

It is apparent from Figure 3 that during the initial stages of hydrogenation (< 10% hydrogenation) the principle reaction occurring is the conversion of alkyne to alkene (Equation 1). Equation 3, the rate expression covering Equation 1, can be rewritten to describe this initial reaction condition (time $\approx$ 0) as follows:

$$\left.\frac{dP}{dt}\right|_{t\approx 0} = - k_1 [A_3] P° \tag{6}$$

where $\left.\frac{dP}{dt}\right|_{t\approx 1}$ represents the initial reaction rate, i.e., change in pressure with time at early stages in the hydrogenation, and P° the initial hydrogen pressure. Therefore, at $t \approx 0$, the value for k_1 can be obtained from a plot of initial reaction rates versus initial hydrogen pressures with the slope being equal to $k_1[A_3]$. Figure 4 presents such data with the resultant value for k_1 being 6.31×10^3 cm^3 mole^{-1} min^{-1}. The value for k_2 (Equations 2 and 5),

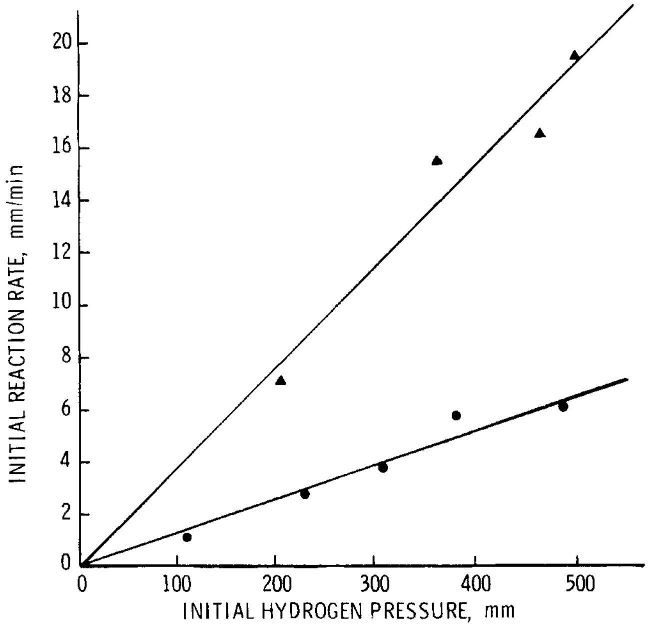

Figure 4. Determination of rate constants using PPE (k_1) and allyl phenyl ether (k_2). PPE data ● and allyl phenyl ether data ▲.

the conversion of alkene to alkane, was determined in the same manner using allyl phenyl ether. In this alkene hydrogen study an allyl phenyl ether/Pd black ratio of 1.66 was used and no PPE was present in the system only neat allyl phenyl ether and catalyst. The value for k_2 was thus determined to be 16.71×10^3 cm^3 $mole^{-1}$ min^{-1}.

The previous result indicates that the hydrogenation of alkyne to alkene (Equation 1) occurs at a slower rate than that of the conversion of alkene to alkane (Equation 2), i.e., $k_1 < k_2$. This result implies that the rate limiting step in the catalytic hydrogenation of phenyl propargyl ether is Equation 1. However, during the hydrogenation of phenyl propargyl ether any allyl phenyl ether formed must principally compete for the catalytic hydrogenation sites with PPE. Consequently, the relative affinities of alkyne versus alkene for these sites could serve to re-define the rate limiting step. An indication of the value for k_2 operative during the hydrogenation of PPE may be obtained from Figure 3 by noting that when the hydrogenation of PPE is approximately 60% completed, then the allyl phenyl ether concentration achieves a transient steady state condition and the rate of change in the concentration of allyl phenyl is zero, i.e., the plateau region in Figure 3 for A_2. Under this transient steady state condition Equation 4 becomes:

$$k_1 [A_3] [P_{H_2}/RT] = k_2 [A_2] [P_{H_2}/RT] \qquad (7)$$

or

$$k_2 = \frac{k_1 [A_3]}{[A_2]} \qquad (8)$$

where $[A_3]$ and $[A_2]$ refer to the concentrations of A_3 and A_2 at 61.8% hydrogenation from Figure 3. The value for k_2 thus obtained is 2.17×10^3 cm^3 mole^{-1} min^{-1}. This value for k_2 differs by nearly a factor of 8, lower than that obtained when the neat catalytic hydrogenation of allyl phenyl ether was studied (2.17×10^3 versus 16.71×10^3 cm^3 mole^{-1} min^{-1}).

Thus, the rate limiting step in the hydrogenation of phenyl propargyl ether is that involved in the conversion of alkene to alkane since it has been shown that in the PPE hydrogenation mileau $k_1 > k_2$. This result is opposite that obtained when k_2 is determined from the neat catalytic hydrogenation of allyl phenyl ether and suggests that it is the stronger adsorption of alkyne on the catalytic sites which causes $k_1 > k_2$. Similar results have been observed during the hydrogenation of acetylene over a palladium catalyst where the hydrogenation of gaseous ethylene commences only after most of the acetylene has been reduced (8). This is attributed to strength of adsorption which decreases in the sequence acetylene > ethylene > ethane or triple bonds > double bonds > single bonds.

This study has also shown the ability of HPLC to completely resolve the three major products of hydrogenation of phenyl propargyl ether. The same column/solvent system developed for phenyl propargyl ether has been successfully applied to the separation of the hydrogenation products of dimerized phenyl propargyl ether (1,6=diphenoxy-2,4-hexadiyne).

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REFERENCES

1. Bond, G. C. and Wells, P. B., "The Hydrogenation of Acetylene. V. The Reaction of Acetylene with Hydrogen and Deuterium Catalyzed by Alumina-Supported Ruthenium and Osmium," J. Catalysis, 12, 157 (1968).

2. Mann, R. S. and Khulbe, K. C., "The Hydrogenation of Ethylacetylene. III. Reaction of Ethylacetylene with Hydrogen Catalyzed by Platinum and Indium," J. Catalysis, 17, 46 (1970).

3. Campbell, K. N. and Campbell, B. K., "The Addition of Hydrogen to Multiple Carbon-Carbon Bonds," Chem. Revs., 31, 77 (1942).

4. Berkowitz, L. M. and Rylander, P. N., "Selective Hydrogenation of Olefins with Ruthenium," J. Org. Chem., 24, 708 (1959).

5. Courtney, R. L. and Harrah, L. A., "Organic Hydrogen Getters. Part 1," J. Material Science, 12, 175 (1977).

6. Trujillo, R. E. and Courtney, R. L., "Organic Hydrogen Getters. Part 2. Hydrogenation Rates of Solid Alkynes on Palldium-Calcium Carbonate Catalysts," J. Material Science, 12, 937 (1977).

7. Anderson, D. R., Courtney, R. L., and Harrah, L. A., Patent No. 3,896,042,22, July (1975).

8. Bond, G. C., *Catalysis by Metals*, Academic Press, New York, NY, 1962, p. 291.