Heterogeneous Catalysis in the Liquid Phase

A STUDY OF SOME OF THE FACTORS AFFECTING ALKYNE HYDROGENATION

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The number of parameters affecting the rate and possibly the mechanism of a liquid phase, heterogeneously catalysed reaction is very much larger than that for the analogous gas phase reaction. The hydrogenation of two alkynes has been studied using a palladium oxide catalyst, in a number of solvents, in order to discover the effect of the latter upon the rates of reaction. It was hoped that results of general applicability to other liquid phase heterogeneously catalysed systems might be obtained. In this context, surface- and diffusion-controlled regimes have been identified, pronounced solvent effects were observed and attempts have been made to measure hydrogen concentrations in solution under reaction conditions.

Acres and Bond (1) have laid the groundwork for a more systematic study of heterogeneous catalytic reactions, where one reactant is in the liquid phase and the other is in the gas phase, and have outlined the number and nature of the parameters involved. Bond and Rank (2) and Russian workers (3, 4) have observed that the selectivity of a given metal in liquid phase hydrogenation of multiply unsaturated hydrocarbons is similar to those observed in the gas phase (5), which suggests that the mechanisms

are the same. However, this may not always be the case.

A number of common organic solvents are reported as being suitable media for liquid phase hydrogenations (6), but little attempt has yet been made to correlate solvent properties with the activity and selectivity of a given type of metal catalyst in a given solvent. This article describes an attempt to remedy some of these discrepancies using one particular type of unsaturated system, namely alkyne hydrogenation over a reduced palladium oxide catalyst.
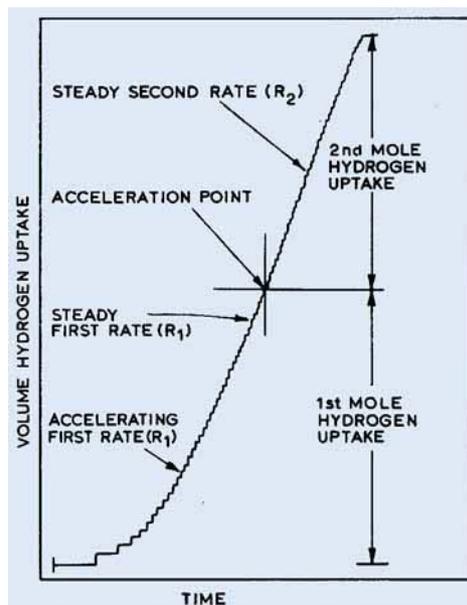

Fig. 1 *Typical volume-time trace for hydrogen uptake. Only the magnitude of the features changes from one solvent to another*

The reactions were carried out in an agitated spherical reaction vessel, connected to an automatic hydrogenator, which maintained the reaction at one atmosphere total pressure, while producing a record of the volume of hydrogen uptake as a function of time. Phenyl acetylene and 1-octyne were the alkynes used and with the exception of temperature and agitation speed studies, the work was carried out at 30°C, 1 atm total pressure and the vessel was shaken at 1,300 vibrations/min. The palladium oxide catalyst was usually reduced in situ but occasionally it was pre-reduced in the solvent before addition of the alkyne.

Gas chromatography was used both in product analysis and in hydrogen solubility measurement; the latter was an adaptation of a method reported by Swinnerton, et al. (7).

Hydrogen Uptake as a Function of Time

The volume-time traces are typified by Fig. 1, this form being common to all solvents. Only the magnitudes of these features change from one solvent to another. The induction period and the duration of the acceleration of the rate R_1 (associated with alkyne to alkene conversion) are undoubtedly solvent dependent. For example, in the n-alcohols, n-hydrocarbons and N : N-dimethyl formamide (D.M.F.), relatively short induction periods (<5 min) and fairly rapid attainment of a steady R_1 value were observed. Rates were measured as ml H_2 STP/min and all rates reported in this article are in accord with this convention.

For the most part, the second rate R_2 (associated with alkene to alkane conversion) was linear until very near the end of the reaction, when R_2 declined towards zero. However, its magnitude and the point at which it declined were solvent dependent.

A pre-reduced system gave rise to values of R_1 and R_2 that were linear but depressed by 30 to 50 per cent compared with the in situ reduced system. The use of 5 per cent palladium on charcoal and palladium black

catalyst resulted in linear R_1 and R_2 values and the difference between R_1 and R_2 was greater with these catalysts.

Gas-liquid chromatographic analysis of the reaction indicated that, in all solvents, the palladium oxide catalyst was very selective for octene production (selectivity $\geqslant 0.95$).

The Rate as a Function of Catalyst Weight

Acres and Bond (1) have proposed, as a necessary criterion for surface control, that the rate should be directly proportional to the catalyst weight and their findings in this respect have been confirmed by Yao and Emmett (8). Furthermore, use of a supported palladium catalyst in this work resulted in similar observations.

The use of a palladium oxide catalyst gave rise to non-linear rate vs. weight plots, whether or not the system was reduced in situ or pre-reduced and much effort was devoted to ensuring that the effect was genuine. Figure 2 shows this effect for phenylacetylene hydrogenation in methanol and n-butanol. These are entirely repre-
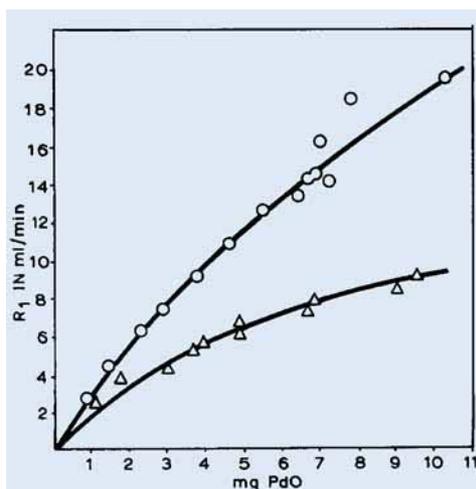
Fig. 2 Rate as a function of catalyst weight for the hydrogenation of phenylacetylene in methanol and n-butanol. Temperature 30°C, pressure 1 atm, frequency 1,300 vibrations/ min

○ *5 per cent v/v phenylacetylene in methanol*
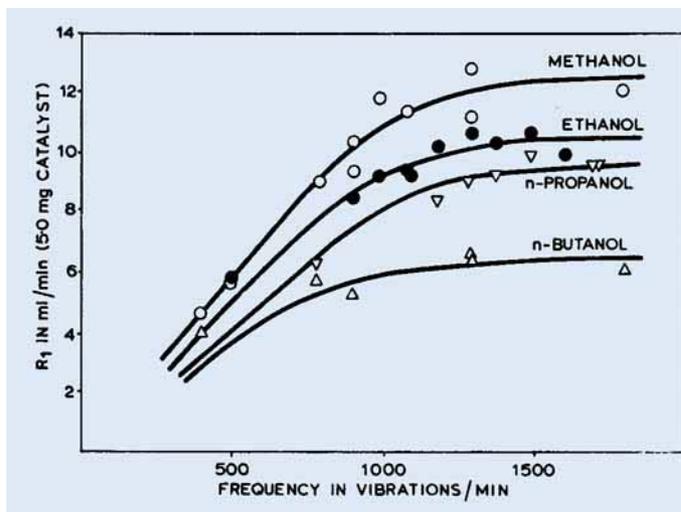△ *5 per cent v/v phenylacetylene in n-butanol*

Fig. 3 Rate as a function of shaking speed for phenyl-acetylene hydrogenation in n-alcohols. Temperature 30°C, pressure 1 atm.

○ 5 per cent v/v phenyl-acetylene in methanol
● 5 per cent v/v phenyl-acetylene in ethanol
▽ 5 per cent v/v phenyl-acetylene in n-propanol
△ 5 per cent v/v phenyl-acetylene in n-butanol

sentative of other solvents and the other alkyne, but the power of the catalyst weight to which the rate is directly proportional is dependent upon solvent and reactant. For example, for phenylacetylene hydrogenation in alcoholic solvents the following values of the above exponent are found; MeOH (0.77), EtOH (0.67), n-PrOH (0.62), n-BuOH (0.55); but for 1-octyne hydrogenation analogous values are MeOH (0.69) and n-PrOH (0.52).

The Rate as a Function of Shaking Speed

A plot of rate against shaking speed shows two distinct features. The first occurs at lower shaking speeds, where the rate is dependent upon shaking speed. The second is that at higher shaking speeds, the rate is constant and independent of shaking speed.

These effects are shown in Fig. 3 and it is also apparent that a solvent effect may be in operation because of the different limiting rates observed in the four alcohols. In three n-paraffin solvents, n-hexane, n-heptane and n-octane, rates were identical, within experimental error, in all three solvents. The limiting rate reached was similar to that in n-butanol but it was achieved at a lower shaking speed (about 700 vibrations/min).

The Effect of Temperature

At high shaking speeds (> 1,200 vibrations/min), the rate of the reaction (R_1 or R_2), when corrected to allow for the progressive de-

Table I
Apparent Activation Energies for Phenylacetylene and Styrene Hydrogenation
(1,300 vibrations/min; 1 atm hydrogen)

Solvent	E (phenylacetylene) kcal/mole	E (styrene) kcal/mole
methanol	8.0	5.8
ethanol	9.2	8.0
n-propanol	7.1	6.3
n-butanol	9.4	7.7
n-heptane	11.0	—

Fig. 4 Rate R_2 as a function of dielectric constant of solvent for 1-octyne hydrogenation. Temperature 30°C, pressure 1 atm, shaking speed 1,300 vibrations/min., solution 5 per cent v/v 1-octyne in solvent

○ methanol
● ethanol
▽ n-propanol
△ n-butanol
▼ acetone
□ methyl ethyl ketone
⁓ acetic acid
⨯ ethyl acetate
◇ n-heptane
■ dioxan
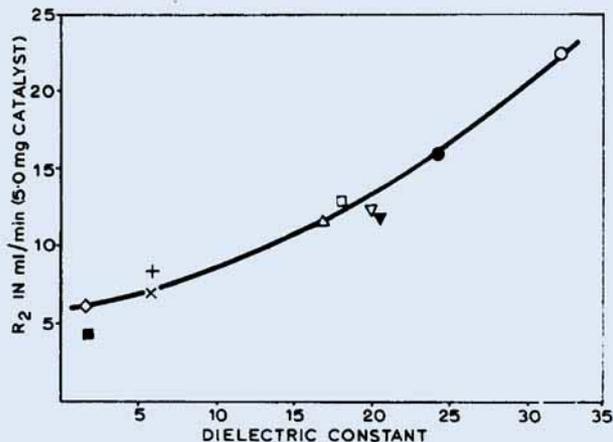
crease of hydrogen partial pressure due to increasing solution vapour pressure as temperature increases, obeyed the Arrhenius equation. The values of the activation energies obtained from the latter, for phenylacetylene and styrene hydrogenation in some solvents are shown in Table I.

The magnitude of these figures is in accord with a surface-controlled process.

At low shaking speeds (400 to 500 vibrations/min), the corrected rates do not obey the Arrhenius relationship or at least they do so only over a very narrow temperature range. In the latter case a measured activation energy of 4 to 5 kcal/mole was usual.

For the most part, the rate was found to be proportional to a power of the absolute temperature, a result that is indicative of diffusional control.

Solvent Effects

The hydrogenation of 1-octyne was studied in a series of solvents at 30°C, 1 atm total pressure and 1,300 vibrations/min. Rates varied quite widely and several physical constants of the solvents were examined to see whether or not the rate of reaction bore any relation to them. In fact, only the dielectric constant proved at all satisfactory and Fig. 4 shows how R_2 varies with the di-
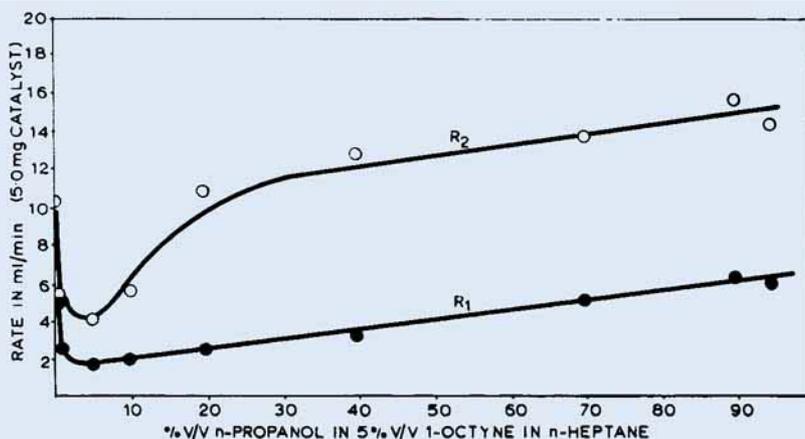

Fig. 5 Rate as a function of solution composition for 1-octyne hydrogenation in n-propanol/n-heptane mixtures. Temperature 30°C, pressure 1 atm, shaking speed 1,300 vibrations/min

Table II		
Bunsen Coefficients* at 30°C (β_{30}) and Zero Time (t_o)		
Shaking Speed vibration/min.	β_{30} at t_o (n-propanol)	β_{30} at t_o (n-heptane)
500	0	0.010
1300	0.013	0.064
† β_{30} at t_∞	0.042	0.085
* ml hydrogen at STP per ml solution	† equilibrium value for a poisoned system	

electric constant of the solvent. R_1 was not chosen because it reached a steady value at different times in different solvents thus making comparison difficult. The values of R_2 for methanol, acetone, and methyl ethyl ketone (M.E.K.) are corrected because of their relatively high vapour pressures even at 30°C. However, there is a reasonable correlation between rate and polarity. The significant exception is N:N-dimethyl-formamide (D.M.F.), which has a large dielectric constant (>110), the rates in this solvent not being any greater than those in the alcohols.

Rate measurements were also carried out in mixed solvent systems. The first of these, n-propanol/n-heptane, proved interesting because a minimum rate was observed at about 5 per cent v/v n-propanol in 5 per cent 1-octyne/90 per cent n-heptane and this is shown in Fig. 5; a pre-reduced system behaved similarly except that the minimum was less marked and occurred at about 10 per cent v/v n-propanol.

A second mixed solvent system D.M.F./methanol gave rates that were a linear function of composition. However, of interest and significance, is the fact that where R_1 increased with D.M.F. content, the R_2 value decreased.

Hydrogen Concentration Measurements

In order to measure hydrogen concentrations the palladium oxide catalyst had to be poisoned using tetrahydrothiophen (T.H.T.) during the second mole of hydrogen uptake; the alkyne was able to compete, to some extent, with the poison and without poison, enough colloidal metal was drawn into the hypodermic syringe from the vessel to deplete the solution of hydrogen before it could be injected into the gas chromatograph. An added complication was that even 12.5 p.p.m. T.H.T. in the solution depressed the normal Bunsen Coefficient (β) for hydrogen by up to 50 per cent.

An identical programme was carried out using a palladium on nylon-66 fibre catalyst, that did not require poisoning because it was possible to avoid drawing it into the syringe.

The results in both systems paralleled each other and it was observed that even in the poisoned palladium oxide system, where T.H.T. depressed Bunsen coefficients, the hydrogen concentration during reaction lay in a range of 75 per cent equilibrium value (n-heptane) to values approaching zero in more polar solvents. These observations refer to a surface controlled system. Under diffusion control, the hydrogen concentration is even smaller, as is indicated in Table II. This shows Bunsen Coefficient measured at 30°C (β_{30}) and these are the results of making a series of measurements at various times under stagnant conditions after poisoning the reaction. The experimental results were extrapolated to zero time (t_0) and are reported in the table.

Discussion

It is suggested that the accelerating value of R_1 is caused by water formed during the reduction of the palladium oxide. The water may compete with alkyne or prevent alkyne from adsorbing quickly on active sites. In other words, there is a time lag before alkyne reaches its proper steady state concentration on the surface and the water disperses into the solvent. This is supported by the fact that R_2 values were often unobtainable in hydrocarbon solvents, in which water is largely immiscible.

Undoubtedly also, the polarity of the solvent affects the rate of reduction of the catalyst and, furthermore, solvents with electron-rich groups can interact with the metal and retard reaction.

The non-linear rate vs. catalyst weight relation seems to be peculiar to the palladium oxide catalyst and may be due to the formation of a surface area that is not directly proportional to the weight of oxide introduced. It is not too difficult to show, assuming that spherical metal particles are produced, that the rate could be proportional to (catalyst weight)$^{2/3}$; in this work, depending upon the solvent (alcoholic and n-paraffin), rate $\propto$ (catalyst weight)$^{0.5-0.7}$.

Both shaking speed and solvent variation (Figs. 3 and 4) indicate definite solvent effects, in that the latter enhances or inhibits rates of reaction, but has little or no effect upon selectivity. Hydrogen solubilities are ruled out as a cause of rate differences in different solvents, since low rates are often observed in solvents that have the largest amount of hydrogen dissolved in them.

That the dielectric constant or polarity of a solvent seems to influence the rate attained in that solvent can be understood, at least qualitatively, in that the formation and dissociation of metal-carbon bonds could well be influenced by solvent polarity. However, other factors must play a part because D.M.F., despite its large dielectric constant, does not give rise to unduly large rates. Possibly it co-ordinates with the metal

surface, thus acting in this respect as an inhibitor.

The occurrence of a minimum rate in the mixed solvent system (Fig. 5) is explicable, partly in terms of the water produced during reduction and partly that at low n-propanol concentrations, the alcohol may co-ordinate with the metal, without providing a medium into which the water can diffuse; evidence has previously been found for such interactions (9).

There are several interesting features of these systems that will provide material for future investigation. The first of these is the physical state of the reduced oxide catalyst in respect of particle size and surface area. Secondly, the minimum rate observed in mixed solvent systems is interesting and this investigation should be extended to already reduced (Pd black) or supported systems (Pd/charcoal). Finally, hydrogen concentration measurements during the course of reaction certainly require more study, both with palladium oxide and supported palladium, and palladium black catalysts, since the results reported here are limited both in extent and by the experimental techniques so far employed.

References

1 G. J. K. Acres and G. C. Bond, *Platinum Metals Rev.*, 1966, **10**, 122

2 G. C. Bond and J. S. Rank, *Proc. 3rd Int. Cong. Catalysis*, 1965, 1225

3 L. Kh. Freidlin and Yu. Yu. Kaup, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1964, (11), 2102

4 Kh. V. Bal'yan and N. A. Borovikova, *J. Gen. Chem. U.S.S.R.*, 1959, **29**, (8), 2520

5 G. C. Bond, "Catalysis by Metals", Academic Press, London and New York, 1962

6 R. L. Augustine, "Catalytic Hydrogenation", Edward Arnold, London, 1965

7 J. W. Swinnerton, V. J. Linnenbom and C. H. Cheek, *Anal. Chem.*, 1962, **34**, 1509

8 H. C. Yao and P. H. Emmett, *J. Am. Chem. Soc.*, 1959, **81**, (10), 4125

9 E. L. McDaniel and H. A. Smith, *Adv. in Catalysis*, 1957, **9**, 76