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Organic hydrogen getters

Part 2 *Hydrogenation rates of solid alkynes on palladium-calcium carbonate catalysts*

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Reaction rates for the hydrogenation of twenty-seven acetylenic materials, both compounds and polymers, on calcium carbonate-supported palladium catalysts are reported. Certain of these organic–catalyst formulations are capable of rapidly and quantitatively removing hydrogen from an environment at low hydrogen pressure (100 mm Hg) and ambient temperature. Analysis of the rate data suggests that inductive, steric, and catalyst poisoning factors are involved in determining the rate of hydrogenation for any given alkyne.

1. Introduction

The hydrogenation of acetylenes at heterogeneous catalytic surfaces has been studied in the gas phase [1–3] and in solution [4, 5]. Such studies have provided insights into the mechanism of alkyne hydrogenation, its stereo-chemical course and the selectivity of the process. Only recently, however, has an investigation into the neat catalytic hydrogenation of alkynes in the solid state been reported [6]. Practical application of this neat hydrogenation of solid alkynes in resolving problems associated with a hydrogen environment, i.e. explosive hazard, malfunction of electrical components, hydrogen embrittlement of metals, has been patented [7]. Further application of this approach for removal or control of hydrogen and its isotopes requires studies of those parameters which influence the course of the catalytic reaction. The present study reports on the effect of chemical substituents on the neat catalytic hydrogenation of solid acetylenes.

2. Experimental

2.1. Hydrogenation protocol

The apparatus used in this study has been described by Courtney and Harrah [6]. Basically, it consists of a Parr Calorimeter bomb, modified to accept a digital thermometer, connected to an absolute pressure gauge. The volume of the apparatus was measured using a calibrated Vol-u-meter (Brooks Instrument Company, Hatfield, Penn., USA) and found to be 3438.4 ml. Hydrogenations were conducted by spreading 0.5 g of a given organic–catalyst formulation over the bottom of a glass container which was then placed inside the calorimeter bomb. After evacuation, the system was back-filled with hydrogen at a pressure of 100 mm Hg. The total hydrogen uptake (pressure drop) and any temperature change were monitored as a function of time until no further pressure change occurred.

2.2. Organic–catalyst preparation

A given alkyne compound (0.33 g) was dissolved in an appropriate solvent, generally tetrahydrofuran, and added to 0.2 g 5% palladium on calcium carbonate (unpoisoned, reduced form-Strem Chemical Inc, Danvers, Mass, USA). The slurry was swirled as the solvent evaporated leaving a coating of the organic over the catalyst substrate. The organic–catalyst mixture was evacuated for 30 min prior to being pulverized and placed in the hydrogenation reaction vessel.

It has been shown [6] that an organic–catalyst formuation between 60 and 65% by weight in organic is not pyrophoric in the presence of both hydrogen and oxygen. Such a formulation is not considered to represent monomolecular coverage of the catalyst by the organic, but rather the amount of organic required to protect the catalyst from rapid oxidation upon exposure to oxygen.

The organic–catalyst ratio for the acetylenic polymers was altered from that used for the acetylenic compounds because the increased molecular weights of the polymers compared to those of the compounds yielded organic coatings on the catalyst which reduced getter efficiency and capacity. It is felt that the increased molecular weights of the polymers hindered the access of hydrogen to the catalyst surface and affected the ability of the hydrogenated polymeric product(s) to migrate from the catalyst surface. Qualitative experiments, similar to those performed on 1,6-diphenoxy-2,4-hexadiyne [6], showed that an organic–catalyst formulation of 15% by weight polymer was not pyrophoric and, consequently, this organic–catalyst ratio was used for the polymeric getter candidates. All further preparation and experimentation involving the acetylenic polymers were accomplished as previously described for the acetylenic compounds.

2.3. Acid chloride preparation

Acid chlorides which could not be purchased commercially (Aldrich Chemical Company, Milwaukee, Wisconsin, USA, or Research Inorganic Chemicals/Research Organic Chemicals Company, Sun Valley, California, USA) were prepared by mixing equimolar amounts of the appropriate acid or diacid with phosphorous pentachloride and collecting the acid chloride distillate under vacuum.

2.4. Compound preparation

The following compounds were obtained commercially (Farchan Chemical Company, Willoughby, Ohio, USA): 2,4-hexadiyne-1,6-diol (I, m.p. 110° C), 1,6-diphenoxy-2,4-hexadiyne (II, m.p. 80° C), 2,7-dimethyl-3,5-octadiyne-2,7-diol (III, m.p. 129° C), 1,8-cyclotetradecadiyne (IV, m.p. 93° C).

The following protocol was used to prepare 2,4-hexadiyne-1,6-diol dibenzoate (V, m.p. 72 to 73° C, lit. m.p. 70 to 71° C), 2,4-hexadiyne-1,6-diol di-*n*-butyrate (VI, oil), 2,4-hexadiyne-1,6-diol diphenylcarbonate (VII, m.p. 107 to 109° C, lit. m.p. 108 to 110° C); 2,4-hexadiyne-1,6 diol di-*n*-octanoate (VIII, oil) and 2,7-dimethyl-3,5-octadiyne-2,7-diol diphenylcarbonate (IX, m.p. 67 to 69° C): 0.01 mol of the alkyne was dissolved in 30 ml acetone and 0.022 mol of the appropriate acid chloride was added with stirring to the ice-cold solution. 4 ml pyridine were added with stirring and the solution was removed from the ice bath and allowed to stir at room temperature for 30 min. Any precipitate formed at this point was removed by filtration. The clear solution or filtrate was poured into water. Solid derivatives formed precipitates at this point and were isolated by filtration and recrystallized. Oily derivatives formed emulsions on addition of water and could be isolated by ether extraction, drying the ether extract over magnesium sulphate, filtering, and evaporation of the ether.

The following protocol was used to prepare 2,4-hexadiyne-1,6-diol bis-phenylurethane (X, m.p. 168 to 170° C, lit. m.p. 172° C) and 2,7-dimethyl-3,5-octadiyne-2,7-diol bis-phenylurethane (XI, m.p. 164 to 165° C): 1.5 g alkyne was dissolved in 10 ml tetrahydrofuran and 5 ml phenylisocyanate were added. 4 to 6 drops of stannous octoate were then added with stirring. A solid mass formed and 100 ml hexane were added with vigorous stirring and the suspension filtered. The product was recrystallized from ethanol.

The preparation of 2,4-hexadiyne-1,6-diol di-toluene-*p*-sulphonate (XII, m.p. 95 to 96° C, lit. m.p. 92 to 94° C) was as follows: 5.5 g alkyne were dissolved in 50 ml tetrahydrofuran and 25 g *p*-toluenesulphonyl chloride were added. The solution was cooled to 15° C and 10 g potassium hydroxide in 80 ml water were added slowly with vigorous stirring. The solution was stirred at room temperature for 4.5 h and then poured into 500 ml ice water. The crystalline product was collected by filtration, washed with ice water and recrystallized from 95% methanol.

The preparation of 1,6-di-iodohexa-2,4-diyne (XIII, m.p. 64 to 65° C, lit. m.p. 64° C) was as follows: 5.0 g sodium iodide were dissolved in 50 ml dry ethanol and 4.5 g XII, dissolved in 20 ml carbon tetrachloride, were added. The solution was kept in the dark for 24 h at room temperature after which water was added and the product was isolated by ether extraction. The ether extract was dried over magnesium sulphate, filtered, and the extract taken to dryness. The product was crystallized from hot hexane.

The preparation of 2,7-dimethyl-3,5-octadiyne-2,7-diol dibenzoate (XIV, m.p. 106 to 108° C) was as follows: 3.0 g alkyne were dissolved in 30 ml pyridine and 10 ml benzoyl chloride were added. The solution was allowed to stand for 24 h; then 40 ml 1-propanol was added and the suspension poured into 300 ml water. An oily yellow residue formed which gradually crystallized. The excess water was poured off and the product was washed with acidified 1-propanol (5 ml conc. HCl per 50 ml 1-propanol).

The preparation of 2,4-hexadiyne-1,6-diol di(cyclohexylcarboxylate) (XV, m.p. 31 to 32° C) was as follows: 2.75 g alkyne were dissolved in 30 ml pyridine and 6.7 ml cyclohexylcarboxylic acid chloride were added to the ice cold solution. The solution was stirred at room temperature for 24 h, then poured into 300 ml water and extracted with ether. The ether extract was dried over magnesium sulphate, filtered, and the yellow filtrate taken to dryness. The oily yellow residue was washed with water to remove the pyridine odour and then dried under vacuum. The waxy solid was recrystallized from acetone. The product sorbed acetone strongly and it was necessary to freeze the acetone residue and then evacuate in order to obtain the waxy solid product.

It was possible to prepare 2,7-dimethyl-3,5-octadiyne-2,7-diol di(cyclohexylcarboxylate)(XVI, m.p. 125 to 127° C) via the same procedure used in preparing XV except that the product, a white solid, was obtained on adding methanol to the dry ether extract and reducing the volume.

The biphenyl propargyl ether (m.p. 80 to 81° C) and 1,6-di-biphenoxyl-2,4-hexadiyne (XVII, m.p. 165 to 166° C) were prepared according to the protocol used in making phenyl propargyl ether and 1,6-diphenoxy-2,4-hexadiyne [6].

The preparation of 2,4-hexadiyne-1,6-diol di-4-biphenylcarboxylate (XVIII, m.p. 87 to 89° C) was as follows: 0.69 g alkyne was added to 2.75 g 4-biphenylcarbonyl chloride dissolved in 20 ml methylene chloride. 1.0 ml *N,N*-dimethylaniline was added drop by drop to the stirred suspension at room temperature and the suspension stirred for 24 h. The solution was taken to dryness and 100 ml hexane were added to the residue. The insoluble fraction was isolated by filtration, dissolved in ether, re-filtered, and the filtrate taken to dryness.

2.5. Polymer preparation

The following protocol was used to prepare the polyesters of 2,4-hexadiyne-1,6-diol and succinic acid (XIX, m.p. 101 to 109° C), sebacic acid (XX, m.p. 70 to 110° C), and 1,4-cyclohexanedicarboxylic acid (XXI, m.p. 90 to 110° C); and the polyesters of sebacic acid with 2,7-dimethyl-3,5-octadiyne-2,7-diol (XXII, m.p. 40 to 60° C), 2,5-dimethyl-3-hexyne-2,5-diol (XXIII, m.p. 64 to 71° C), 3-hexyne-2,5-diol (XXIV, m.p. 50 to 55° C) and 2-butyne-1,4-diol (XXV, m.p. 37 to 43° C): 0.025 mol alkyne was dissolved in 50 ml acetone and 0.025 mol of the appropriate diacid chloride was added to the solution. 4 ml pyridine were added to the solution with stirrring and the precipitated material was poured into 150 ml water. The product was isolated by filtration.

The polyester (XXVI, m.p. 65 to 75° C) of phthalic acid and 2,4-hexadiyne-1,6-diol were prepared as follows: 1.1 g alkyne and 1 g sodium hydroxide were dissolved in 50 ml water and 5 drops triethylamine were added to the solution. While vigorously stirring the solution, 30 ml methylene chloride were added followed by the addition, drop by drop, of 30 ml methylene chloride containing 1.6 ml *O*-phthalic acid chloride. The solution was stirred for 2 h after the addition of 5 additional drops of triethylamine. The organic layer was washed with three 200 ml portions of water and once with 100 ml water containing 3 ml phosphoric acid. Additional water washings were employed until a pH of 5-7 was obtained.

The organic layer was poured into 600 ml 2-propanol and the white suspension allowed to stand in ice for 4 h. The precipitate was isolated by filtration, re-dissolved in acetone, filtered, and the filtrate taken to dryness.

The polycarbonate (XXVII, m.p. 81 to 95° C) of 2,4-hexadiyne-1,6-diol was prepared as follows: 5.5 g alkyne were dissolved in 15 ml tetrahydrofuran and 6 ml dimethyl carbonate added to the solution. 0.3 g sodium was added and the mixture heated for 2 h with a distillate coming off at 40 to 45° C. 100 ml hexane were added to the distillation flask and the precipitate was dissolved in 15 ml tetrahydroduran, purified using carbon black and the filtrate taken to dryness.

2.6. Product characterization

The infra-red spectra were taken for all derivatives prepared using a Perkin-Elmer, Model 21, double-beam infra-red spectrometer. The absence of a hydroxil absorption band at 3550 cm^{-1} and the concomitant appearance of a carboxyl absorption band at 1745 cm^{-1} for compounds V–XI, XIV, XV, and XVIII–XXVII was taken as evidence that the appropriate derivative had been prepared. In a similar manner, the appearance of sulphonate absorption at 1210 and 1178 cm^{-1} for compound XII and of iodo absorption at 1140 cm^{-1} for compound XIII, when coupled with an absence of hydroxyl absorption, was taken to mean that the appropriate compound had been prepared.

The gel permeation chromatograms (GPC) were done on a Waters' Associates ALC/GPC-502/401 dual detector liquid chromatograph (Waters Associates, Milford, Mass.) equipped with a M/6000 solvent delivery system and a Model U6K liquid injector. The columns (7 mm i.d. x 30 cm) were standard Waters' μ Styragel. These columns were placed in series according to the following polystyrene contour chain-length exclusion limits: 10^4, 10^3, 500, 500, 100 and 100 Å. The 10^4 Å column was on the first column connected to the chromatograph. The solvent, tetrahydrofuran (uninhibited re-distilled from Burdick and Jackson Labs, Muskegon, Michigan), was maintained at a rate of $2\,\mathrm{ml\,min^{-1}}$. This combination of columns and flow rate yielded a column pressure of 2000 psi*. A calibration curve was developed in the normal manner using polystyrene standards (Waters Associates). The GPC chromatograms of alkynes XXIII, XXIV, and XXV were obtained by preparing $20\,\mathrm{mg\,ml^{-1}}$ samples of each alkyne in tetrahydrofuran (THF) and injecting $100\,\mu$l of each of the solutions into the chromatograph. All three samples showed a broad molecular weight distribution centred about a peak which corresponded to the elution volume for a 3000 molecular weight polystyrene standard.

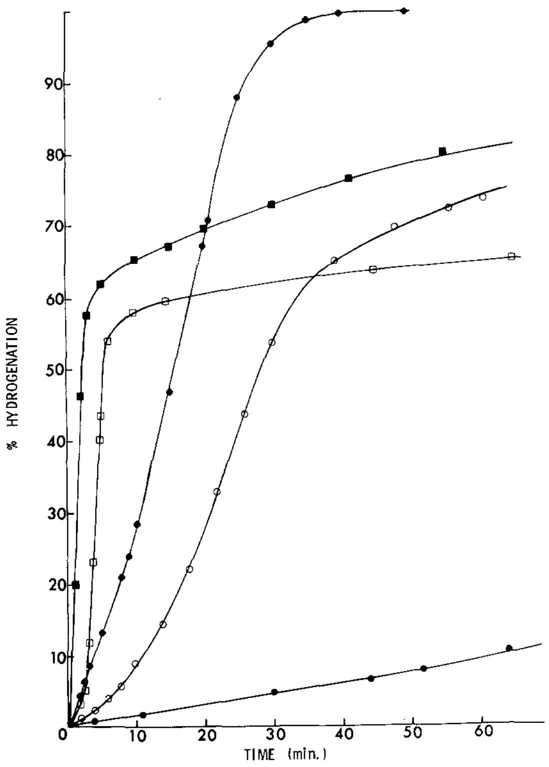

Figure 1 The hydrogenation of various alkynes: compound II, ♦; compound XV, ■; compound VIII, ●; polymer XIX, □; polymer XXI, ○.

3. Results

The various organic–catalyst formulations were prepared as described in Section 2.1 and placed in the calorimeter reaction vessel. The reaction vessel was evacuated and back-filled with hydrogen to a pressure of 100 mm Hg and the volume of hydrogen taken up (pressure drop) together with any temperature changes were periodically recorded. A temperature rise of approximately 1 to 4° C was observed to precede the hydrogenation reaction with the rate of temperature increase paralleling the rate of hydrogenation.

Fig. 1 illustrates the type of hydrogenation data which was obtained. Clearly, the neat heterogeneous hydrogenation of alkynes is not a uniform process for all organic–catalyst formulations. The hydrogenation curves varied as to the presence or absence of induction times, hydrogenation rate, the extent of hydrogenation, i.e. percent hydrogen uptake based on amount of acetylenic material present. This variability in the shapes of the various hydrogenation curves (Fig. 1) was observed with both acetylenic compounds and polymers.

Fig. 2 presents data on the hydrogenation of varying ratios of 2,4-hexadiyne-2,4-diol diphenylcarbonate (VII) on the 5% palladium/calcium carbonate catalyst. Varying the organic–catalyst ratio for this acetylenic material serves to alter the shapes of the hydrogenation curves which are generated. Both the induction time and extent of hydrogenation appear to be influenced by the ratio of organic to catalyst. However, over a 24 h period each of the four formulations exhibited more than a 90% uptake of hydrogen based on the amount of acetylenic material available for hydrogenation. Hence, the apparent variation in extent of hydrogenation noted in Fig. 2 does not represent the actual course of hydrogenation. The times required for these formulations to achieve the 90% hydrogenation level was directly related to the organic–catalyst ratio.

While the induction times of the hydrogenation

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* $10^3\,\mathrm{psi} \equiv 6.89\,\mathrm{N\,mm^{-2}}$.

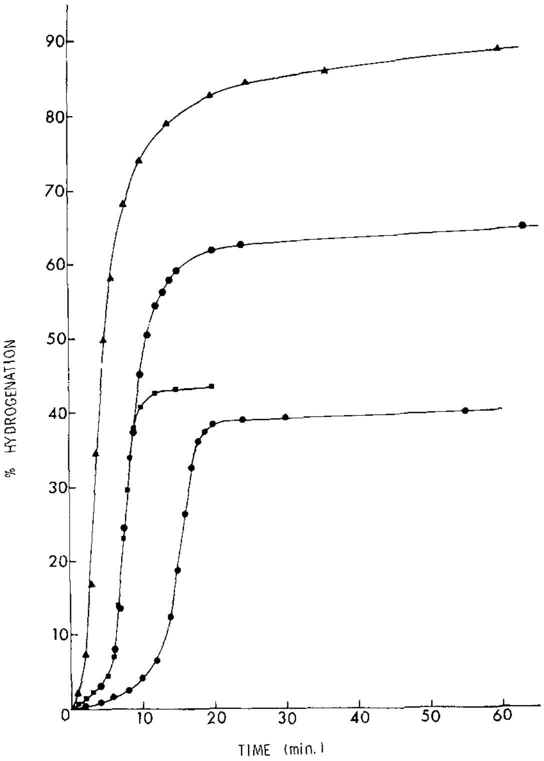


Figure 2 The hydrogenation of varying ratios of 2,4-hexadiyne-2,4-diol diphenyl-carbonate (VII) on 5% palladium/calcium carbonate catalyst. All samples contained 0.2 g catalyst with varying wt% alkyne: 45% alkyne, ▲; 55% alkyne, ●; 62% alkyne, ■; 67% alkyne, •.

curves for the same acetylenic material varied depending on the organic–catalyst ratio, the maximum hydrogenation rate (maximum slope, Fig. 2) was essentially the same for each of these formulations. This observation is considered to be of importance because it suggests that comparison of the maximum hydrogenation rates between different acetylenic compounds and polymers is valid. Since the catalyst weight remained at 0.2 g, a change in wt% organic meant that the various formulations (Fig. 2) represented different mole ratios of organic to catalyst. The fact that these different mole ratios of organic to catalyst exhibited equivalent maximal hydrogenation rates (Fig. 2) suggests that comparisons of hydrogenation rates between *different* alkynes can be considered. Different alkynes, at the same wt% organic–catalyst ratio (Section 2.2), would yield different mol% organic–catalyst ratios but their maximal hydrogenation rate would be independent of mole ratios of organic to catalyst considerations (Fig. 2).

TABLE I Kinetic data for alkyne hydrogenation

Alkyne number	Maximum rate (mm H_2/mol organic/sec)	Hydrogenation (%)
I	7.1	33
II	14.4	100
III	8.4	96
IV	186.8	92
V	74.5	96
VI	0.9	100
VII	39.6	100
VIII	1.9	94
IX	33.7	44
X	No reaction (18.9)*	–
XI	No reaction	–
XII	No reaction	–
XIII	No reaction	–
XIV	7.1	100
XV	13.1	98
XVI	3.6	100
XVII	No reaction	–
XVIII	21.4	100
XIX	54.0	94
XX	67.7	84
XXI	7.2	100
XXII	13.0	66
XXIII	6.8	34
XXIV	18.7	100
XXV	122.8	76
XXVI	46.1	100
XXVII	72.2	100

* Rate using palladium black as catalyst

Table I presents a summary of the hydrogenation data obtained for each alkyne studied.

4. Discussion

The neat heterogeneous hydrogenation of alkynes at ambient temperature and low hydrogen pressures, appears generally feasible according to the data presented in this study (Table I). The advantages of such hydrogen gettering formulations are that:

(1) the hydrogen getters (organic–catalyst combinations) are passive systems requiring no external energy sources for initiation;

(2) the hydrogen getters can be incorporated into closed systems, e.g. placed in bags, distributed as powders, painted on surfaces;

(3) the hydrogenation of acetylenic materials using a heterogeneous catalyst is essentially an irreversible process and results in extremely low hydrogen equilibrium concentrations [6].

The major limitation of these hydrogen gettering systems is their stability relative to the environment in which they are to function. For example, the 1,6-diphenoxy-2,4-hexadiyne (II) has been extensively studied [6] and shown to be a stable and efficient getter. However, exposure of this hydrogen getter to temperatures above its melting point would result in altered catalyst coverage with subsequent loss in gettering capacity. Other conjugated acetylenic getter candidates (V, XXV, XXVII) while more reactive than II have been found to undergo polymerization through the triple bonds leading to brightly coloured products with diminished gettering capacity. This polymerization process can be initiated by either heat, ultraviolet radiation, or gamma radiation [8, 9].

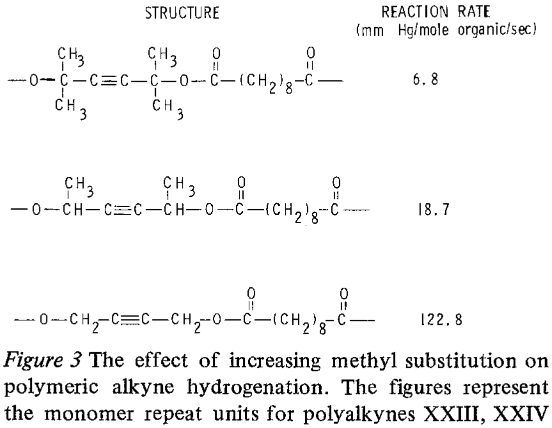
The development of chemically stable gettering systems also depends upon adequate coating of organic material onto the catalyst surface. The concomitant presence of hydrogen, oxygen and palladium catalyst can result in the exothermic formation of water via a pyrophoric reaction. Studies of this phenomena *vis á vis* the organic–catalyst system considered here showed that the pyrophoric reaction could be eliminated by a suitable coating of organic over the catalyst surface [6]. This coating functions as a barrier to the rapid, simultaneous presence of hydrogen and oxygen at the catalyst surface. Therefore, all compounds (I to XVIII) reported in this study employed a ratio of 62% organic (wt/wt) to 38% catalyst (wt/wt) in order to prevent this pyrophoric reaction.

Fig. 2 illustrates that the shape of hydrogenation curves depends upon the organic to catalyst ratio. In all cases the extent of hydrogenation was greater than 90% but the times required for the various formulations to reach these levels varied as the amount of organic present, i.e. more organic relative to catalyst required longer times. At the highest organic–catalyst ratio there is observed a prolonged induction time which could correspond to the slower rate of diffusion of hydrogen through the organic layer. This formulation required the longest time to reach the 90% hydrogenation level. The intermediate organic–catalyst ratios showed a shortened induction time but the same general sigmodial shaped curve as the highest organic–catalyst ratio. The lowest organic–catalyst ratio showed nearly no induction time. Of importance is the fact that all formulations showed essentially the same maximal hydrogenation rates (maximum slope, Fig. 2). This observation suggests that the rate of hydrogenation at the catalyst surface depends only on the presence of catalyst, hydrogen and organic and when these components are in the proper juxtaposition the reaction proceeds uniformly. The fact that the maximal hydrogenation rates are not of equal duration suggests that the flow of hydrogenated product from the catalyst surface and the movement of acetylenic material towards the catalyst is slower the greater the organic–catalyst ratio, and this results in a less than optimum concentration of hydrogen, catalyst and alkyne being present at any given instant.

Fig. 2 illustrates that while differently shaped hydrogenation curves can be generated for a given getter formulation the values for the maximum hydrogenation rates are equivalent. This observation is stressed because it serves to justify a comparison of the maximum hydrogenation rates for all hydrogen getter candidates studied even though the shapes of their individual hydrogenation curves were different (Fig. 1).

Comparing the maximum rate data for the various compounds and polymers (Table I) suggests certain trends regarding the chemical requirements for a given acetylenic compound to effectively function as a hydrogen getter. The role of electron-donating substituents in influencing the hydrogenation rate of acetylenes is best illustrated by comparing the polymeric materials XXIII, XXIV, and XXV (Fig. 3). In this series the only variable was a change in the number of methyl groups associated with the acetylenic portion of the polyester.

The positive inductive effect associated with methyl substituents is well known and the data can be interpreted as indicating that increasing electron density about the acetylenic portion of the getter results in a less effective gettering material. Conversely, the increased bulkiness of



$-O-C(CH_3)_2-C\equiv C-C(CH_3)_2-O-C(=O)-(CH_2)_8-C(=O)-$

$-O-CH(CH_3)-C\equiv C-CH(CH_3)-O-C(=O)-(CH_2)_8-C(=O)-$

$-O-CH_2-C\equiv C-CH_2-O-C(=O)-(CH_2)_8-C(=O)-$

Figure 3 The effect of increasing methyl substitution on polymeric alkyne hydrogenation. The figures represent the monomer repeat units for polyalkynes XXIII, XXIV and XXV.

the molecule with increasing methyl substitution should assist hydrogenation by reducing the adsorption of the acetylene which by competitive exclusion of hydrogen can retard the hydrogenation reaction [10]. Therefore, the diminished gettering capacity of the more highly methylated polyester is probably a reflection of positive inductive effects decreasing hydrogen gettering activity, i.e. hydrogenation rate. Additional evidence for this conclusion is provided by comparing the same derivatives of the 2,4-hexadiyne-1,6-diol and 2,7-dimethyl-3,5-octadiyne-2,7-diol getter formulations (V versus XIV, VII versus IX, and XV versus XVI). In general, the octadiyne derivatives took up hydrogen at a significantly lower rate than the equivalent hexadiyne derivative.

If substituents which donate electrons, positive inductive effects, result in poor gettering materials, then substituents which withdraw electrons should result in good gettering candidates. This expectation can be examined by comparing the maximum hydrogenation rates for the hexadiyne-diol derivatives in Fig. 4. Comparing compounds I and II shows that the ability of the unsaturated carbon atom, the phenyl group in this case, to attract electrons increases the hydrogenation rate of the diphenoxy derivative (II) by a factor of two over the hexadiyne-diol (I). It is pertinent to note that replacement of an α-hydrogen in acetic acid by a vinyl or phenyl group increases the acidity of the compound also by a factor of about 2 in each case [11].

Carbonyl groups are also known to exhibit negative inductive effects [11] and the effect of such a substitution is illustrated by XV. Once again the introduction of an electron withdrawing group into the acetylenic material increases the hydrogenation rate by about a factor of 2. The di-cyclohexyl derivative was chosen so as to approximate the steric volume of the di-phenoxy derivative and thus allow a more direct comparison of carbonyl versus phenyl substitution on hydrogen uptake.

The effect of combining the carbonyl and phenyl substitution in the same acetylenic compound is shown by comparing compound V with I, II and XV. The di-benzoyl derivative takes up hydrogen about a factor of 5 times greater than the carbonyl or phenyl substituents alone and more than 10 times faster than the 2,4-hexadiyne-1,6-diol. In addition, the observation that the di-biphenoxy derivative (XVII) did not take up hydrogen, while the carbonyl containing di-biphenyl derivative (XVIII) did function as a hydrogen getter, implies an activating role for electron withdrawing groups attached to the acetylenic molecule. However, the large decrease in melting point between the di-biphenyl and the carbonyl containing di-biphenyl derivatives indicates that introduction of the carbonyl group strongly influences the packing behaviour of the biphenyl molecule. Conceivably, a physical packing alteration could also influence the adsorption of the biphenyl derivative on the catalyst surface and thereby influence its hydrogenation behaviour.

The importance of the hydrogen being able to penetrate the organic layer in order to catalytically hydrogenate the organic material is illustrated by comparing the rate data for alkynes VI, VII, and XV in Table I. The solid di-ester hexadiyne derivative (XV) was able to take up hydrogen at a greater rate than the liquid di-ester hexadiyne derivatives (VI and VIII). Compounds VI and VIII were viscous oils and it is felt that the slow rate of hydrogen uptake by these compounds was caused by a diffusion limited process involving the penetration of the hydrogen through the oil to the catalyst surface. A solid alkyne coated over the catalyst surface is considered to be more porous and therefore more permeable to the hydrogen than a viscous oil. These materials (VI, VIII, and XV) contained aliphatic carbonyl substituents and

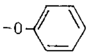
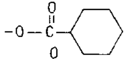
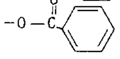
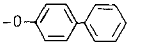
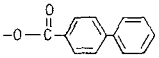
ALKYNE NUMBER	R GROUP	REACTION RATE	M. P.
I	–OH	7.1	110 C
II		14.4	80 C
XV		13.1	31 C
V		74.5	72 °C
XVII		NO RX	165 C
XVIII		21.4	87 C

Figure 4 The effect of substituents on alkyne hydrogenation. The substituents (R) were various symmetrical derivatives of the diacetylene R–CH$_2$–C≡C–C≡CH$_2$–R.

could have been expected to take up hydrogen at nominally the same rate were it not for the suggested hydrogen permeability factor.

The physical nature of acetylenic materials apparently can influence the hydrogenation rate of the material by establishing a physical permeability barrier to the hydrogen. In addition, the chemical nature of the acetylenic material can also be detrimental to the hydrogenation process. The compounds in Fig. 5 were prepared because it was felt the negative inductive effects they could potentially provide might make them hydrogen gettering candidates. The fact that compounds X, XII, and XIII did not take up hydrogen is ascribed to the poisoning of the catalyst by the nitrogen, sulphur and iodo moities present in the respective molecules. Of interest is the observation that compound X did take up hydrogen if in place of 5% palladium on calcium carbonate an equivalent weight of pure palladium black was used as catalyst. Such a finding supports the idea that poisoning of the catalyst was a factor in the lack of gettering activity of compounds X to XIII. Nitrogen, halogen, and sulphur moities are known to act as catalyst poisons [12, 13].

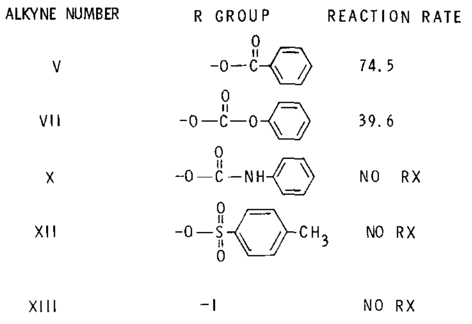


Figure 5 The effect of substituents on alkyne hydrogenation. The substituents (R) were various symmetrical derivatives of the diacetylene $R{-}CH_2{-}C{\equiv}C{-}C{\equiv}C{-}CH_2{-}R$. Alkyne X was hydrogenated (Table I) when palladium black was used as the catalyst.

Mention has been made of the appropriate juxtaposition of hydrogen, alkyne and catalyst for optimal hydrogenation efficiency. The ability of hydrogen to penetrate the organic layer was also considered as a requirement for effective hydrogenation of the acetylene. A third component of the hydrogenation reaction could be the movement of hydrogenated product away from the catalyst surface and migration of fresh acetylenic material into the reaction zone on the catalyst surface. Compound IV, 1,8-cyclotetradecadiyne, was screened as a getter candidate and was found to be most efficient of all the materials studied with a maximum hydrogenation rate of 186.8 mm H_2/mol organic/sec. The open cyclic structure of this material perhaps allows a less hindered diffusion of hydrogen to the site of hydrogenation on the catalyst surface. In addition, this material undergoes a change in ring structure as the triple bonds are reduced to double and finally to single bonds. Fig. 6 illustrates the type of transition that Dale *et al.* [14], consider to be occurring in the reduction of 1,8-cyclotetradecadiyne. This change in structure could allow the hydrogenated product to flow from the reaction zone and fresh acetylenic material to migrate into the catalytically active region more readily. Whatever the explanation, this material achieves the highest hydrogen rate

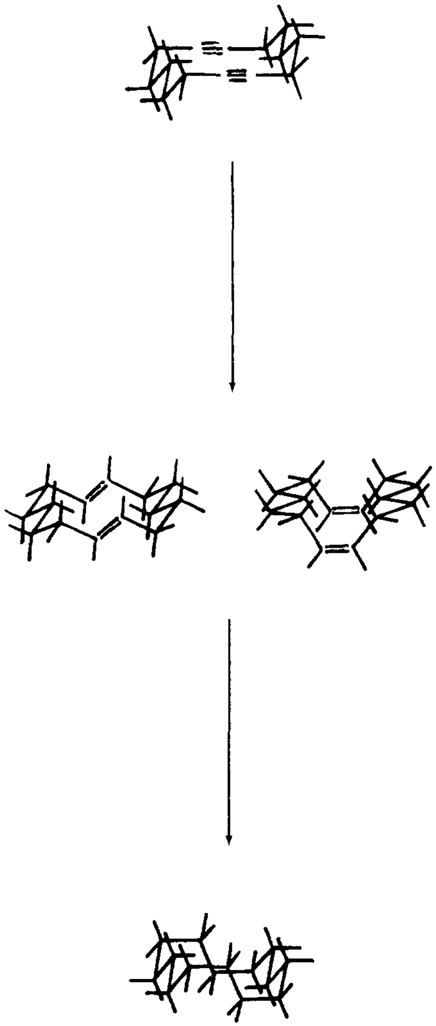


Figure 6 The structural changes associated with the hydrogenation of 1,8-cyclotetradecadiyne (IV).

without the necessity of a conjugated di-acetylenic system or recourse to inductive effects arguments and thus emphasizes that the physical nature of the reactants and products *vis á vis* the catalyst surface are extremely important in defining the success of the neat heterogeneous hydrogenation of acetylenic materials.

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