SEMIHYDROGENATION OF ACETYLENES

MODIFIED LINDLAR CATALYST†

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Abstract—The effect of doping Lindlar catalyst with different metal salts (shown in Table 1) on selectivity, during semihydrogenation of some acetylenes to the corresponding olefins, has been studied. Lindlar catalyst modified with $MnCl_2$ has been found to be more selective and reproducible.

Catalytic semihydrogenation[1] of an acetylenic linkage is a valuable synthetic operation and a variety of heterogeneous catalysts based on palladium,[1,2] platinum,[1,3] rhodium[1,3c] or nickel,[1,4] often further modified for improved selectivity by addition of other metal salts and/or amines, sulphides, have been employed. In recent years, a number of homogeneous catalysts and heterogenised homogeneous catalysts have been evaluated for the same purpose.[2b,5] However, Pd–CaCO₃–PbO catalyst, known as Lindlar catalyst,[6] remains by far the most commonly used catalyst for the purpose, although doubts have been expressed[7] on its advantages over other catalysts. We now report a modified Lindlar catalyst which, at least in the systems investigated, has clearly demonstrated improved selectivity for semihydrogenation.

During another investigation, it was observed that Lindlar catalyst, prepared[6b] by using lead acetate of laboratory reagent grade quality, was more selective than the one obtained by using analytically pure lead acetate; indeed the recommended procedure[6b] calls for commercial grade of lead acetate! It was reasonable to surmise that trace impurities in the laboratory reagent grade lead acetate were responsible for this difference in the selectivity. There appears to be no report in the literature about the effect of metal ions on the activity of Lindlar catalyst. A systematic study was thus undertaken to identify the metal ion(s) capable of improving the selectivity of this catalyst for semihydrogenation. This way it was also hoped to get at a more reproducible preparation of the catalyst.[8]

According to Maxted,[9] metal ions which have the five *d*-orbitals immediately preceding *s* or *p* valency orbitals occupied by electron pairs or at least by single unpaired electrons are toxic to platinum group catalysts, whereas those with their outermost *d*-orbitals empty or partly filled are non-toxic. Since Lindlar catalyst is essentially a poisoned Pd catalyst, we used the above empirical rule to select metal ions in a bid to further refine the performance of Lindlar catalyst. Cu^{2+}, Cd^{2+}, Hg^{2+}, Sn^{2+}, Mn^{2+}, Fe^{3+}, Co^{2+} and Ni^{2+} salts were selected from the first category, whereas a Ba^{2+} salt was evaluated from the second category. This list includes possible metal salt impurities (Cu, Fe) believed to be present in the laboratory reagent grade lead acetate used by us in the first preparation of Lindlar catalyst; the list also includes some of the metal ions (Cu, Cd, Hg, Sn) evaluated singly by Lindlar[6a] and rejected in favour of lead. Chlorides of these metals were used for the purpose. A block pre-paration of Lindlar catalyst[10] was made using analytical grade reagents; this material, in different portions, was then doped with these salts as detailed under Experimental, to get catalysts (Lindlar–MXn) for evaluation.

RESULTS

In the first instance phenylacetylene was selected as the substrate for evaluation of different catalysts. The results are summarised in Table 1 and Fig. 1: Table 1 emphasises the selectivity of the catalysts as compared to that of Lindlar catalyst (entry 1), while Fig. 1 gives the rates of hydrogenation. It is clear from these data that Lindlar catalyst is not very selective: about 11% over-reduction to ethylbenzene took place before hydrogenation rate showed a clear break. On the other hand, doping with $CdCl_2$, $SnCl_2$, $NiCl_2$, $CuCl_2$ or $MnCl_2$ led to significant improvement in selectivity. It may be noted that all these metal ions, according to Maxted,[9] are palladium catalyst poisons; $BaCl_2$ (Table 1, entry 2) which would fall in the category of non-toxic ions, failed to improve selectivity to any significant extent. $FeCl_3$ affected the activity adversely, while with $HgCl_2$ and $CoCl_2$ modified catalysts, hydrogenation was too sluggish and remained incomplete.

To further explore the scope of these modified catalysts, semihydrogenation of dehydronerolidol (1) was investigated and the results have been briefly summarised in Table 2. As can be seen, the Lindlar–MXn catalysts exhibited much superior performance as compared to the Lindlar catalyst. From a comparison of data in Tables 1 and 2, $MnCl_2$ appeared to be superior to other salts, as it gave uniformly good results both with phenylacetylene and with dehydronerolidol, and hence was selected for further evaluation on a few other acetylenes. Results of these experiments are summarised in Table 3. These results clearly demonstrate better selectivity with Lindlar–$MnCl_2$ catalyst for all the monosubstituted acetylenes investigated; in a single example of a disubstituted acetylene (5) the performance of Lindlar–$MnCl_2$ catalyst was at par with that of the Lindlar catalyst.[11,12] Figure 2 depicts the rate studies of semihydrogenation of these substrates (1–5) for both these catalysts; the lower rates of hydrogenation with Lindlar–$MnCl_2$ are consistent with the higher selectivities achieved.

As already indicated in the footnote to Table 1, all these hydrogenations were carried out in the presence of quinoline (secondary poison in Lindlar's recipe), which is known[6] to aid selectivity. To evaluate the importance of the secondary poison in the case of Lindlar–$MnCl_2$ cata-

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Table 1. Evaluation of different modified Lindlar catalysts for semihydrogenation[a] of phenylacetylene

No	Doping salt	Product composition (%) and selectivity at 1 mole H_2 absorption				Product composition (%), selectivity and mole equivalent H_2 absorbed at "full"[b]hydrogenation				
		ϕ-C≡CH	ϕ-CH=CH$_2$	ϕ-CH$_2$-CH$_3$	Selectivity[c]	Selectivity[c]	ϕ-C≡CH	ϕ-CH=CH$_2$	ϕ-CH$_2$-CH$_3$	Mole equiv H_2
1	-	1.2	97.1	1.7	98.3	89.0	0.0	89.0	11.0	1.11
2	BaCl$_2$	1.8	96.3	1.8	98.1	91.0	0.0	91.0	9.0	1.09
3	CuCl$_2$	2.0	95.5	2.5	97.4	94.0	0.0	94.0	6.0	1.06
4	CdCl$_2$	0.5	99	0.5	99.5	97.5	0.0	97.5	2.5	1.025
5	HgCl$_2$	-	-	-	d	d				
6	SnCl$_2$	1.2	97.4	1.4	98.6	97.0	0.0	97.0	3.0	1.03
7	MnCl$_2$	1.3	97.3	1.3	98.6	98.2	0.0	98.2	1.8	1.018
8	FeCl$_3$	2.5	94.0	3.5	96.4	85.0	0.0	85.0	15.0	1.15
9	CoCl$_2$	-	-	-	d	d				
10	NiCl$_2$	1.0	97.5	1.5	98.5	95.7	0.0	95.7	4.3	1.043

[a] Hydrogenation conditions: ϕ-C≡CH (0.01 mole), catalyst (50 mg), quinoline (200 mg), solvent (heptane, 20 ml), temp. 25± 0.1°, pressure (atmospheric).

[b] "Full" hydrogenation implies, when no more H_2 was absorbed or the reaction became exceedingly sluggish.

[c] Selectivity (%) = $\dfrac{\text{Amount of styrene formed}}{\text{Amount of phenylacetylene consumed}}$ × 100

[d] very sluggish and incomplete
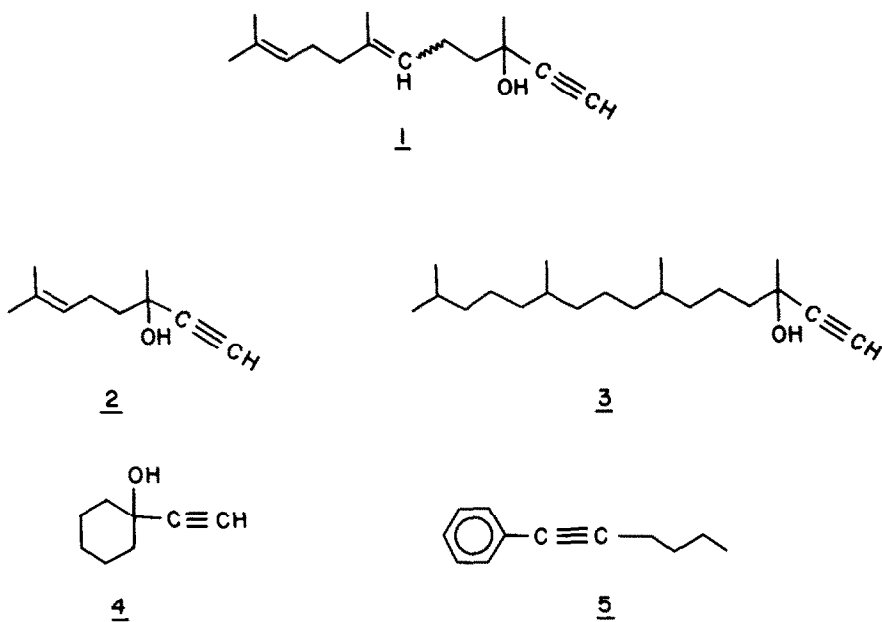
lyst, experiments (substrate: dehydronerolidol) using Lindlar and Lindlar-MnCl₂ catalysts were carried out, but without incorporating quinoline in the reaction mixture. As is clear from the results (Table 2, entry 7,8) selectivity was adversely affected, though much more in the case of Lindlar catalyst. In another set of experiments (substrates: phenylacetylene, dehydronerolidol)

when an additional amount of Pb(OAc)₂·3H₂O equivalent to the amount of MnCl₂–4H₂O used for doping, was incorporated in the preparation of the Lindlar catalyst and the material evaluated for semihydrogenation, selectivity decreased (e.g. see entry 9, Table 2), as compared to that obtaining with Lindlar-MnCl₂ catalyst. In a still another series of experiments,
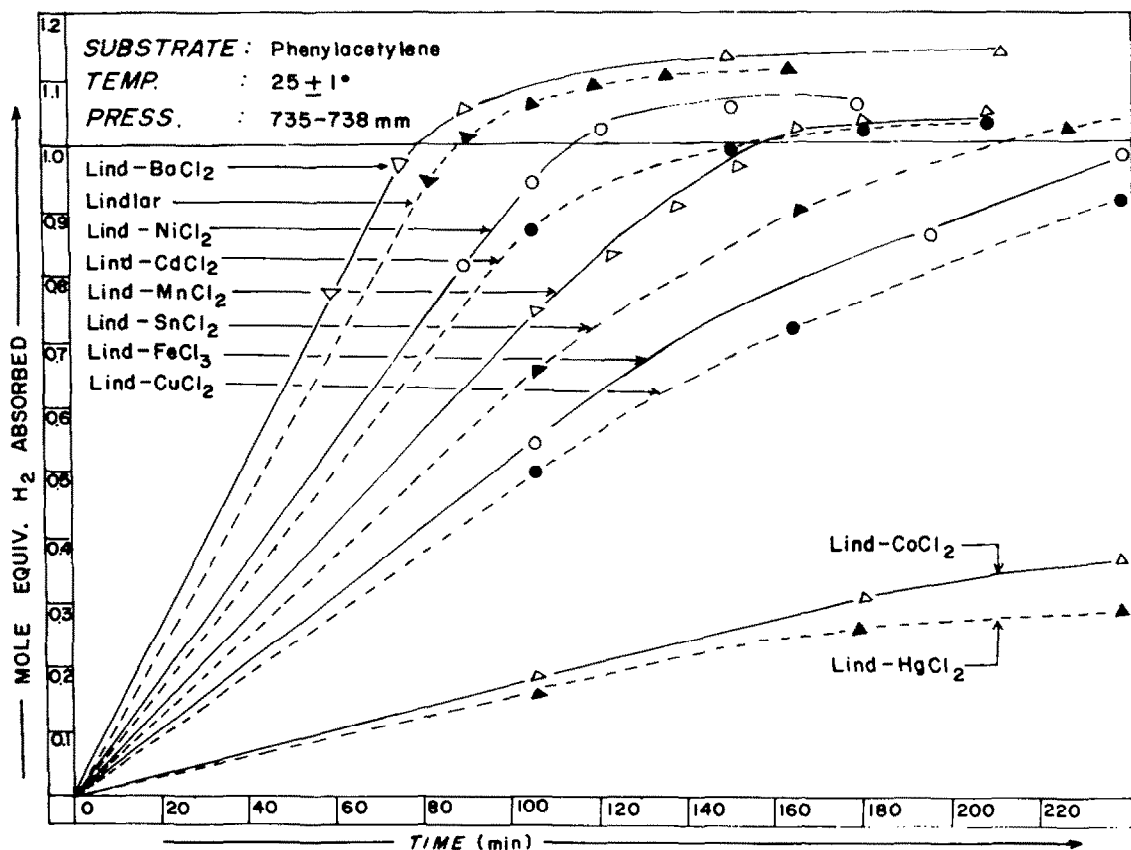

Fig. 1. Rates of hydrogenation of phenylacetylene over different catalysts.

Table 2. Evaluation of different catalysts for the semihydrogenation of dehydronerolidol (1)[a,b]

No	Catalyst	Quinoline	Selectivity (%)	
			at 1.0 mole equiv. H_2 absorption	at "full" H_2 absorption
1	Lindlar	+[c]	93.3	79.0
2	Lindlar - $CuCl_2$	+	94.2	93.0
3	Lindlar - $CdCl_2$	+	95.0	91.0
4	Lindlar - $MnCl_2$	+	99.3	98.5
5	Lindlar - $FeCl_3$	+	95.0	93.0
6	Lindlar - $CoCl_2$	+	95.6	90.0
7	Lindlar	-	88.7	46.0
8	Lindlar - $MnCl_2$	-	92.0	87.0
9	Lindlar with additional Pb^{2+}	+	96.6	88.0
10	$MnCl_2$-Pd-$CaCO_3$	+	88.2	5.0
11	Pd-$CaCO_3$	-	87.3	6.0

[a] See footnotes to Table 1

[b] Dehydronerolidol; trans/cis ratio = 1.17

[c] + indicates, quinoline was used as secondary poison; - indicates its absence.

Table 3. Selectivities in semihydrogenation of some acetylenes over Lindlar and Lindlar–MnCl₂ catalysts[a]

No	Acetylene	Selectivity (%)			
		Lindlar		Lindlar-$MnCl_2$	
		A[b]	B[b]	A	B
1	Dehydrolinalool (2)	95.2	78.0	98.2	97.0
2	Dehydroisophytol (3)	88.6	84.0	97.8	96.4
3	1-Ethynylcyclohexanol (4)	91.4	76.0	97.5	96.8
4	1-Phenylhex-1-yne (5)	-	91.0	-	91.0

[a] See footnotes to Table 1

[b] A = selectivity at 1.0 mole equiv. H_2 absorption
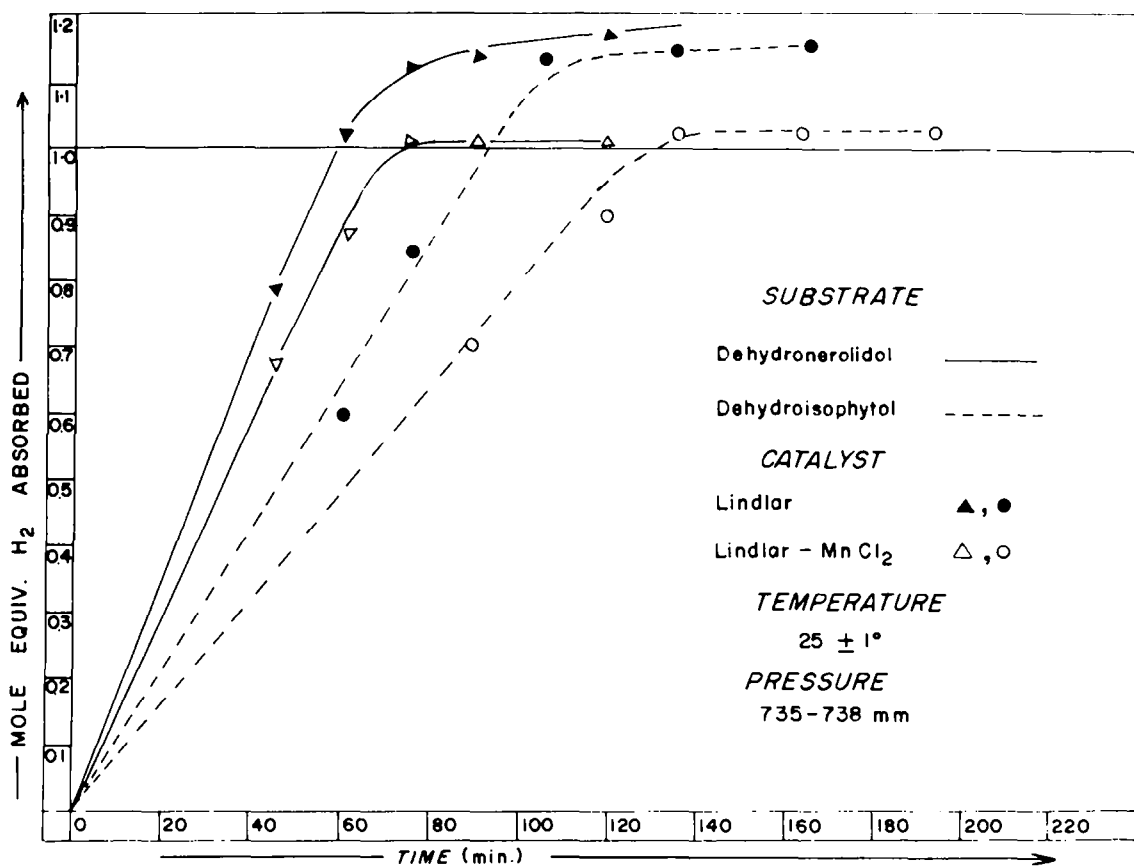
B = selectivity at "full" H_2 absorption.

Fig. 2. Rates of semihydrogenation of dehydronerolidol and dehydroisophytol over Lindlar and Lindlar-MnCl₂ catalysts.

lead acetate was omitted and a $MnCl_2$–Pd–$CaCO_3$ catalyst containing Mn^{2+} equivalent to the $Pb(OAc)_2$ used in the conventional Lindlar catalyst was prepared; this catalyst was quite non-selective for dehydronerolidol (Table 2, entry 10) even at one mole equivalent H_2 absorption, and there was practically no break in hydrogenation around this point leading to as much as 95% over-reaction at the end. For comparison, data for Pd–$CaCO_3$ as a catalyst, has been included in Table 2.

From all these studies we conclude that Lindlar-$MnCl_2$ catalyst is clearly superior to Lindlar catalyst, especially for the semihydrogenation of monosubstituted acetylenes. A secondary poison such as quinoline appears to be essential for good selectivity for this catalyst as well.

DISCUSSION

The mechanism of hydrogenation of acetylenes, especially acetylene itself, has been subject of extended investigations.[13] Of the transition metals, Pd has been found to be most active and selective.[14] Though, it is known[13a,b] that the rate of hydrogenation of an olefin over a Pd catalyst is several times higher than that of the corresponding acetylene, in a competitive reaction, the acetylene gets preferentially reduced because of its higher[15] heat of adsorption, which enables it to displace olefin from the catalyst surface.[16] Thus, acetylenic compound acts, in a way, essentially as a "poison" for the olefin hydrogenation. Both π-adsorbed (6) and doubly σ-bonded (7) structures have been considered[13a,c] for

adsorbed acetylenes. Intermediates 8,[13a] 9,[13c] 10[13d] (Fig. 3) have been proposed for product development. While 8 lies on the pathway to the olefin, 9 and 10 have been suggested as additional (besides 11, arising from chemisorption of the olefin, product of semi-hydrogenation) species leading to the fully reduced product; of course 10 is valid only for mono-substituted acetylenes and has been proposed as an intermediate in the hydrogenation of acetylene at low acetylene coverage and high hydrogen partial pressure.

The role of partially poisoned catalysts (e.g. Lindlar catalyst) and secondary poisons (e.g. quinoline) is not only to improve selectivity, which would diminish as semihydrogenation of acetylene proceeds, but also to inhibit, to varying degree of success, further hydrogenation of the olefin, after disappearance of the acetylene. There is experimental evidence that secondary poisons, such as amines, sulphur derivatives, carbon monoxide (or other compounds carrying hetero atoms with unshared pair of electrons)[18] drastically reduce the rates of hydrogenation of olefins, while leaving the rates of hydrogenation of acetylenes, largely, unaffected.[19] It has been suggested that such compounds are able to displace olefins, but not acetylenes, from the catalyst surface.

The effect of metal ions on the activity of transition metal catalysts, though known[9] for a long time, the precise mechanism of their action is not clearly understood.[20] However, it has been demonstrated[9b] that these metal ions (e.g. Pb^{2+}) in poisoned platinum group cata-
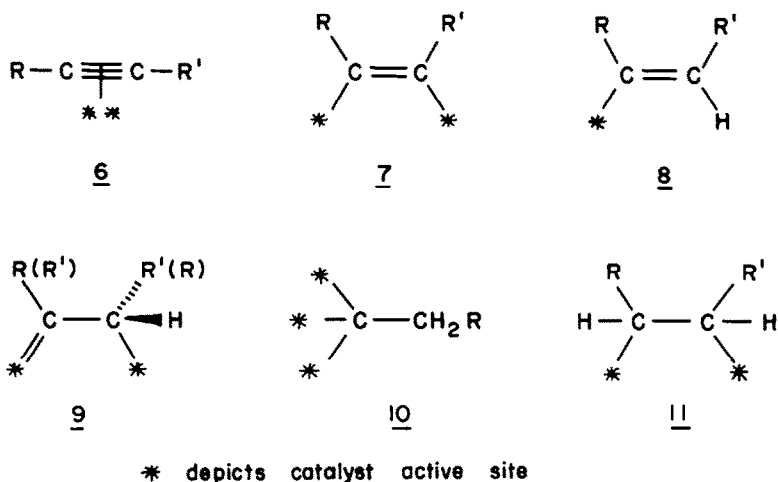
* depicts catalyst active site

Fig. 3. Possible reactive intermediates during hydrogenation of acetylenes.

lysts do not get reduced (during hydrogenation) to zerovalent forms, and it has been suggested that these ions, by interaction of their d-electrons form intermetallic bonds at Pd surface and cause obstructive occupation of the catalyst surface.[9]

A comparison of selectivities at "full" H_2 absorption for Pd–CaCO$_3$ (6%; Table 2, entry 11), and Pd–CaCO$_3$–PbO (46%; Table 2, entry 7) shows that doping with PbO reduces the number of sites active for olefin hydrogenation. Further improvement in selectivity occurs when Pd–CaCO$_3$–PbO catalyst is treated with MnCl$_2$ (87%; Table 2, entry 8). A still further enhancement of selectivity takes place when this catalyst is used in presence of a secondary poison, such as quinoline (98.5%; Table 2, entry 4). The last result is readily understood in terms of what has been stated earlier regarding the role of a secondary poison. To rationalise the steady improvement in selectivity, in going from Pd–CaCO$_3$ to Lindlar to Lind–MnCl$_2$, we would first like to make the following two reasonable assumptions: (i) ensemble of active sites necessary for acetylene to olefin hydrogenation is *different*[21,22] from the ensemble for the reaction $\diagup\!\!\!C\!=\!C\diagdown\!\! \rightarrow \diagdown\!\!C\!-\!C\diagup$, (ii) the distribution of metal cations chemisorbed on catalyst surface is flexible.[23]

As a result of modern techniques of surface analysis, it is now known that a catalyst surface, at the atomic level, is non-uniform and consists of various topographically distinct, non-identical sites (termed terraces, steps, kinks etc), distinguishable by their number of nearest neighbours.[24] Such sites are characterised by different reactivities. It is suggested that Pb^{2+} occupies catalyst surface in such a way that ensembles crucial for olefin hydrogenation are involved. Hydrogenation of C≡C to HC=CH proceeds on ensembles of sites available for this reaction, as well as from restructuring of the Pb^{2+} distribution, which should be possible because of higher heats of adsorption of acetylenes, this restructuring generating some ensembles suitable for HC=CH hydrogenation. Once C≡C → HC=CH reaction is essentially over, Pb^{2+} cations readjust to original distribution, thus essentially blocking ensembles suitable for olefin hydrogenation.[25] The rate differential between the redistribution process and the HC=CH → CH$_2$–CH$_2$ reaction will determine the extent of

over-hydrogenation. The role of ions like Mn^{2+} would then be to reinforce Pb^{2+} distribution in such a way that redistribution is inhibited; this should reduce the rate of semihydrogenation, but improve the selectivity, as observed (Fig. 1). Improvement in selectivity even at one mole hydrogenation (*cf* entries 7/8· and 1/4, Table 2) after treatment of the catalyst with Mn^{2+} should be the result of blocking of sites responsible for direct conversion of C≡C to H$_2$C–CH$_2$ by way of intermediates such as 9. On this model, Co^{2+} and Hg^{2+}, which severely curtail the rate of hydrogenation, would do so by blocking C≡C bond hydrogenation ensembles. An answer to why a particular metal cation behaves in a way it does (Tables 1 and 2) will have to be sought in terms of atomic volume of these ions, their redox potential and more concrete and precise knowledge about the nature of the active sites on Pd catalyst surface.

EXPERIMENTAL

Acetylenes. Phenylacetylene[26] and 1-phenylhex-1-yne[27] (5) were prepared by known procedures and their purities were established by GLC (Table 4 for conditions).

α-Ethynylcarbinols were prepared by the condensation of acetylene with suitable ketones essentially according to the method of Smith;[28] dehydronerolidol (1 mixture of *E*- and *Z*-isomers): yield 90%, b.p. 110–116/1 torr (lit.[29] b.p. 105–110/1 torr); dehydrolinalool (2): yield 86%, b.p. 65°/2 torr (lit.[29] b.p. 87–89/12 torr); dehydroisophytol (3, mixture of isomers): yield 91%, b.p. 132–140/0.7 torr (lit.[29] b.p. 122–23/0.25 torr); 1-ethynylcyclohexanol (4): yield 84%, b.p. 80–82°/18 torr (lit.[30] b.p. 74°/14 torr).

Palladium on calcium carbonate was prepared[6b] from freshly precipitated CaCO$_3$ and palladium chloride (containing 60% Pd and procured from Arora–Matthey Limited, Calcutta, India).

Metal salts. The following analytically pure reagent grade metal salts were purchased from different suppliers and used without further purification for the preparation of modified Lindlar catalysts: Pb(OAc)$_2$ · 3H$_2$O, SnCl$_2$ · 2H$_2$O, NiCl$_2$ · 6H$_2$O and BaCl$_2$ · 2H$_2$O from Sarabhai M Chemicals, Baroda, India; MnCl$_2$ · 4H$_2$O, HgCl$_2$, CuSO$_4$ · 5H$_2$O and Cu(NO$_3$)$_2$ · 3H$_2$O from Pfizer Limited, Bombay, India; CoCl$_2$ · 6H$_2$O from S.D's Lab-Chem Industry, Bombay, India and CdCl$_2$ · 2½H$_2$O from P.P.H. Polskie Odczynniki Chem. Gliwice, Poland.

Laboratory reagent grade of CuCl$_2$ · 2H$_2$O (Sarabhai M. Chemicals) was crystallized from water and FeCl$_3$ (B.D.H. Chemicals, Bombay, India) was sublimed in an atmosphere of chlorine before use.

Lindlar catalyst. A stock batch of Lindlar catalyst was pre-

pared, using analytically pure lead acetate, essentially according to the procedure described[6b] and was used for the preparation of other modified Lindlar catalysts.

Another catalyst (0.5 g) containing 0.387 mmol of lead acetate/g of 5% Pd on $CaCO_3$ catalyst was similarly prepared (and labelled Lindlar with additional Pb^{2-}, Table 2, entry 9).

Modified Lindlar catalysts. A number of modified Lindlar catalysts incorporating different metal salts (0.15 mmol/g of Lindlar catalyst) were prepared by the general procedure described below.

Lindlar catalyst (0.5 g) was stirred with 5 ml soln of a metal salt (0.075 mmol) in water at 92–95° for 1 hr. The contents were cooled to room temp (30°) and diluted with 5 ml water. After allowing it to stand at room temp for 15–16 hr, it was filtered, washed with water (10 ml × 5) and dried at room temp under vacuum (100 torr) over P_2O_5 for 6 hr and stored in a desiccator over silica gel.

$MnCl_2$–Pd–$CaCO_3$ catalyst. It was prepared by treating Pd–$CaCO_3$ (1.0 g) with $MnCl_2 \cdot 4H_2O$ (77 mg, 0.387 mmol) according to procedure described above.

Quinoline. Quinoline (100 g, Koch-Light, England, L.R. grade) was stored over KOH (20 g, L.R. grade) for one week. It was then decanted off and distilled and stored over molecular sieves 4A (15 g, activated at 200° for 3 hr).

n-Heptane. n-Heptane (3.5 l) was stirred at room temp (30°) with 1:1 mixture of conc H_2SO_4 and conc HNO_3 (500 ml) for 6 hr. It was washed with water (200 ml × 3), 5% KOH (150 ml × 4) and water (200 ml × 7), dried (Na_2SO_4) and distilled, b.p. 98–100°. The distilled material was passed through a column (30 cm × 5 cm) of alumina (500 g; activated at 430–450° for 4 hr and 450–500° for 6 hr).

Procedure

In a 2-necked r.b. flask fitted with a rubber septum, were placed the acetylenic compound (0.01 mole), catalyst (50 mg) and quinoline (200 mg) mixed in 20 ml of n-heptane. The flask was dipped in a water bath maintained at 25 ± 0.1°. The flask was

alternately evacuated and filled with H_2. The operations were repeated three times. The contents were stirred, in an atmosphere of H_2, at a constant speed over a magnetic stirrer. The absorption of H_2 was measured periodically (every 15 min), the stirring momentarily stopped and samples (0.3 ml) withdrawn. Hydrogenation was continued till absorption of H_2 essentially ceased.

To ensure reproducibility, all hydrogenations were carried out twice.

Product analysis

The samples withdrawn at different intervals during different hydrogenations were analysed by GLC (Table 4) on Hewlett–Packard 5712A and 7624A gas chromatographs (Al columns, 0.6 cm dia; support, 60–80 mesh Chromosorb W; carrier gas H_2, 60 ml/min). The products of hydrogenation were identified by coinjection with authentic samples. The products of hydrogenation of ethynylcarbinols (1–4) could be analysed only by using two columns: Carbowax 20M column resolved alkynes from alkenes and alkanes, and SE-30 column resolved alkynes and alkenes from alkanes.

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Table 4. GLC analyses of products of hydrogenation of some acetylenes

No	Acetylene, RRT	RRT of products of hydrogenation		GLC conditions[a]
		alkene	alkane	
1	Phenyl acetylene, 1.0	0.60	0.28	A, 100°
2	Dehydronerolidol (**1**, Z/E), 1.0, 1.13	0.6,0.78	0.6,0.78	B, 190°
	1.0, 1.13	1.0,1.13	1.22,1.33	D, 170°
3	Dehydrolinalool (**2**), 1.0	0.58	0.58	A, 170°
	1.0	1.00	1.27	C, 150°
4	Dehydroisophytol (3,isomers) 1.0, 1.19	0.65,0.76	0.65,0.76	B, 200°
	1.0, 1.14	1.0, 1.14	1.23,1.35	D, 170°
5	1-Ethynylcyclohexanol(**4**), 1.0	0.42	0.42	A, 170°
	1.0	1.00	1.17	D, 150°
6	1-Phenylhex-1-yne (**5**), 1.0	0.52	0.41	A, 170°

[a] A = 10% Carbowax 20M, 3.6 m; B = 5% Carbowax 20M, 1.8 m; C = 10% SE-30, 1.8m; D = 5% SE-30, 1.8 m.

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[8]The recommended procedure[6b] for the preparation of Lindlar catalyst results in a catalyst of variable activity, as in the test procedure prescribed, absorption of the first 0.02 mole of H_2 for the hydrogenation of phenylacetylene (0.02 mole) may require 10–90 min. The present work clearly indicates the importance of other metal ions on the activity of Pd–$CaCO_3$–PbO catalyst. Since the procedure[6b] calls for a commercial grade of Pb(OAc)$_2$–3H_2O in the preparation of the catalyst, and since the quality of commercial grade lead acetate is likely to vary within wide limits, this may be *one* of the factors responsible for the varying activity of different preparations.

[9a]E. B. Maxted, *Adv. Catal.* **3**, 129 (1951); [b]E. B. Maxted, *J. Chem. Soc.* **1987** (1949); [c]E. B. Maxted and K. L. Moon, *Ibid.* 2171 (1949).

[10]Strictly speaking Lindlar catalyst is to be prepared[6b] using commercial grade Pb(OAc)$_2$ · 3H_2O. However, since the present study is aimed at evaluating the effect of additional metal ions, we have prepared the catalyst from analytical grade reagents. This preparation will be still called Lindlar catalyst.

[11]The stereoselectivity in the hydrogenation of this substrate is also the same for both these catalysts.

[12]In a private communication (Dr. A. P. S. Narula, Columbia University, New York), we were informed that Lindlar–$MnCl_2$ showed a much superior selectivity as compared to that possible with Lindlar catalyst, in the semihydrogenation of (i)

$$O-Si{+}$$
$$Me-CH-C{\equiv}C-C{\equiv}C-CH_2OH$$
(i)

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[14]See e.g.: G. C. Bond and P. B. Wells, *J. Catal.* **5**, 65 (1966).

[15a]G. C. Bond, *Catalysis by Metals*, pp. 281–309. Academic Press, New York (1962); [b]J. R. Anderson and B. G. Baker, *Chemisorption and Reactions on Metal Films*, pp. 148–150. Academic Press, New York (1972).

[16]However, in some recent studies involving ^{14}C-tracer, it has been found that ethylene adsorption and hydrogenation occurred in the presence of acetylene, and no displacement of ^{14}C-labelled ethylenes was observed.[17] In a still later study[13d] it was shown that the partial pressure of acetylene plays an important role in selectivity; at higher acetylene pressure, hydrogenation of ethylene ceases completely and at the same time acetylene is converted only to ethylene.

[17a]A. S. Al-Ammar, S. J. Thomson and G. Webb, *Chem. Commun.* 323 (1977); [b]A. S. Al-Ammar and G. Webb, *J. Chem. Soc. Faraday I* **74**, 195, 657 (1978).

[18]See e.g.: J. Petro, *Contact Catalysis* (Edited by Z. G. Szabo and D. Kallo), Vol. II, p. 65. Elsevier, Amsterdam (1976).

[19a]T. Fukuda and T. Kusama, *Bull. Chem. Soc. Japan* **31**, 339 (1958); [b]F. J. McQuillin, W. O. Ord and P. L. Simpson, *J. Chem. Soc.* 5996 (1963).

[20]See e.g.: D. Kallo, *Contact Catalysis* (Edited by Z. G. Szabo and D. Kallo), Vol. I, p. 364. Elsevier, Amsterdam (1976).

[21]It is not unreasonable to assume that because of differences in bond length and geometry, the *same* ensemble of active sites may not be suitable for the two reactions. However, on an unadumbrated (Pd) catalyst surface, this poses no limitation on the requirements for the two reactions, as ensembles suitable for both reactions ought to be available.

[22]See e.g.: W. M. H. Sachtler, *Catal. Rev.* **14**, 193 (1976); W. M. H. Sachtler and P. A. Vansanten, *Adv. Catal.* **26**, 69 (1977).

[23]See e.g.: A. K. Galwey, *Ibid.* **26**, 247 (1977).

[24]See e.g.: [a]G. A. Somorjai, *Ibid.* **26**, 1 (1977); [b]*Idem.*, *Angew. Chem. Int. Edn.* **16**, 92 (1977).

[25]In an attempt to experimentally verify this proposal, nerolidol was subjected to hydrogenation in presence of Lindlar catalyst when selectivity at "full" hydrogeneration was found to be 19% compared to 46% with dehydronerolidol (Table 1). It therefore appears that some olefin–Pb^{2+}–Pd surface clusters irreversibly adsorbed on the catalyst surface are also responsible for the inhibition of hydrogenation of olefins.

[26]H. Freisselmann and K. Sasse, *Chem. Ber.* **89**, 1775 (1956).

[27]J. R. Johnson, A. M. Schwartz and T. L. Jacob, *J. Am. Chem. Soc.* **60**, 1882 (1938).

[28]E. F. Smith, U.S. Pat. 2,385,547, Sept. 25, 1945.

[29]L. Blaha and J. Weichet, *Chem. listy* **52**, 753 (1958).

[30]J. H. Saunders, *Organic Synthesis* (Edited by E. C. Horning), Coll Vol. III, p. 416. Wiley, New York (1967).