Base as a Selectivity Agent of Palladium Catalysts in Hydrogenation of 3,7-Dimethyl-6-octen-1-yn-3-ol

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The hydrogenation of 3,7-dimethyl-6-octen-1-yn-3-ol was studied at temperature 60 °C and pressure 0.34 MPa using palladium on calcium carbonate catalysts. The presence of strong base inhibited the consecutive reaction of the desirable hydrogenation product 3,7-dimethyl-1,6-octadien-3-ol.

Catalytic hydrogenation of 3,7-dimethyl-6-octen-1-yn-3-ol (*I*) in the presence of suspended palladium catalysts yields 3,7-dimethyl-1,6-octadien-3-ol (*II*) and 3,7-dimethyl-6-octen-3-ol (*III*) (Scheme 1). Compound *II* is used in perfume industry, compound *III* is undesirable by-product.

carbonate deactivated by lead and quinoline under low pressure in 1-octene gave *II* with 95 % selectivity, in case of parallel reaction in n-octane it was 66 % [4]. High selectivity and nearly 100 % yield of *II* were achieved at hydrogenation in cyclohexane at 10—20 °C under pressure up
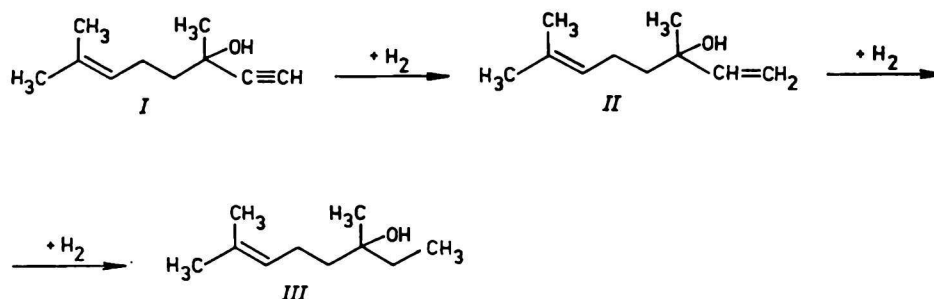
Scheme 1

Catalytic hydrogenation of *I* is most frequently carried out at temperature in the range 20—60 °C under pressure up to 0.5 MPa in organic solvents using colloidal palladium or palladium on supports. Selectivity of the formation of *II* on colloidal palladium in C_2—C_5 alcohols at 30 °C under atmospheric pressure was 84.2—90.5 % [1], by adding pyridinium bases in the presence of palladium halides in alkanes or alcohols at temperature from – 20 to 50 °C under pressure up to 5 kPa selectivity 83.6—98.9 % was achieved [2]. Selectivity of the formation of *II* using 2.8 % palladium on carbon in ethyl alcohol or octane at 20 °C under atmospheric pressure was less than 80 %, using 0.5 % palladium on calcium carbonate deactivated by lead it was 99—99.5 % [3]. Hydrogenation in the presence of 5 % palladium on calcium

to 0.5 MPa by 4 % palladium on calcium carbonate deactivated by metals of the group IIa or IIIb in the presence of pyridine [5]. At the hydrogenation under atmospheric pressure in C_2—C_5 alcohols using 5 %, 2 %, and 0.5 % Pd/Al_2O_3, selectivity of the reactions was 84—90 % [6], 96—99.5 % [1], and 99—100 % [6], respectively. Alkynols were selectively hydrogenated by platinum, palladium or rhodium catalysts preferably supported on a suitable nonacidic carrier such as $BaCO_3$, $CaCO_3$, $BaSO_4$ and charcoal in the presence of alkaline material into corresponding alkenols in high purity and yield [7].

In this study we investigated the dependence of the reaction velocity and overall selectivity of hydrogenation on the mass ratio of the catalyst, base and compound *I*, on temperature and hy-

drogen pressure, and other parameters important for modelling the catalytical process in an isothermal batch suspension autoclave.

EXPERIMENTAL

Catalysts 6 % Pd/CaCO₃, 0.6 % Pd/CaCO₃, 5 % Pd + 5 % Pb/CaCO₃, and 0.5 % Pd + 0.5 % Pb/CaCO₃ were prepared according to [8].

The contents of compounds *I—III* were determined by GC analysis on MEGA SERIES 5300 (C. Erba) apparatus equipped with FID detector using capillary column (diameter 0.5 mm, length 25 m) packed with Carbowax 20 M, at the column temperature 80—120 °C, injection port temperature 210 °C and detector temperature 210 °C (compounds *I—III* with min. content of 99 % rectified by GC were used as analytical standard). Moreover, the content of *I* was determined by alkalimetric titration of nitric acid released by the reaction of acetylenic group hydrogen with silver nitrate solution [9].

Hydrogenation Procedure

A mixture of *I* (304 g, min. content of 96 % by GC), petroleum ether (300 cm³), catalyst (0.32—2.0 g), and base (0—2.0 g) was hydrogenated in a low-pressure isothermic hydrogenator. In time periods filtered samples (< 2 % total volume) were withdrawn from the reaction mixture.

RESULTS AND DISCUSSION

Plots of reaction mixture composition *vs.* time at various mass ratios of 0.6 % and 6.0 % Pd/CaCO₃ to *I*, various amount of substance ratio of KOH to Pd, various pressure and temperature are illustrated in Figs. 1—7.
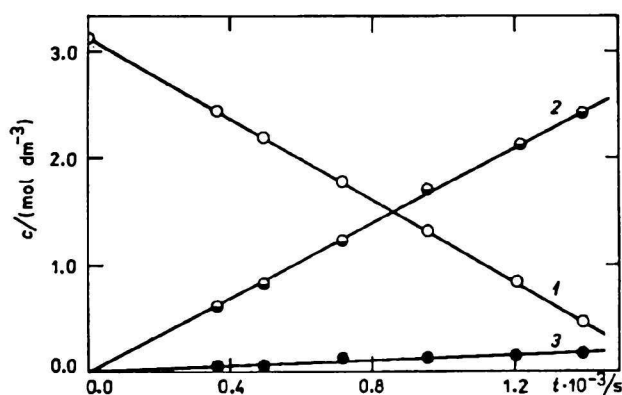

Fig. 1. Concentration dependence of compounds on time at temperature 60 °C, pressure 0.34 MPa and mass ratio of 0.6 % Pd/CaCO₃ to *I* is 6.6 x 10⁻³. *1. I, 2. II, 3. III*.
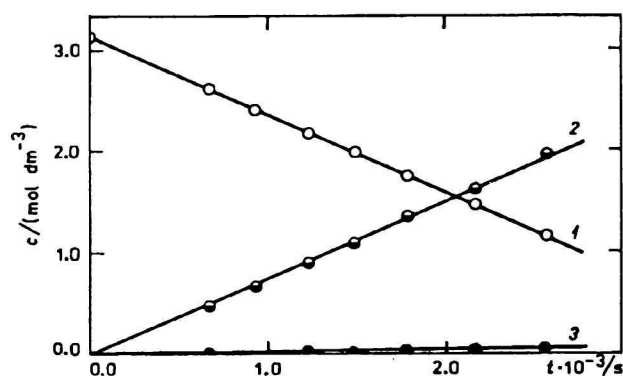

Fig. 3. Concentration dependence of compounds on time at temperature 60 °C, pressure 0.34 MPa, mass ratio of 0.6 % Pd/CaCO₃ to *I* 6.6 x 10⁻³ and mole ratio of KOH to Pd 1.58 x 10². *1. I, 2. II, 3. III*.
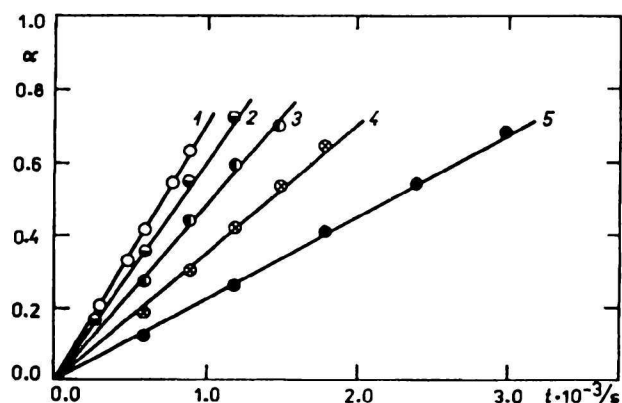

Fig. 2. Conversion degree of *I vs.* time at temperature 60 °C, pressure 0.34 MPa and various mass ratios of 0.6 % Pd/CaCO₃ to *I*: *1.* 8.2 x 10⁻³, *2.* 6.6 x 10⁻³, *3.* 4.9 x 10⁻³, *4.* 3.3 x 10⁻³, *5.* 1.6 x 10⁻³.
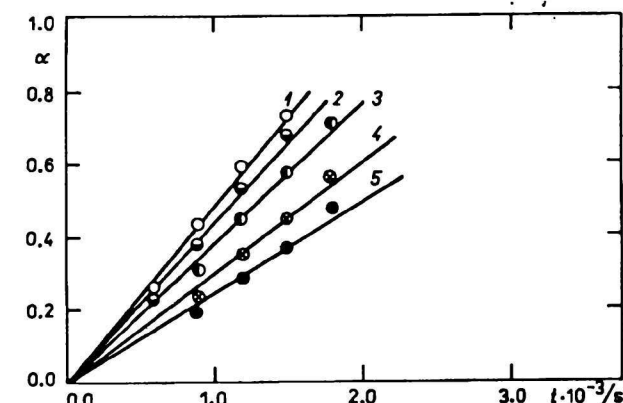

Fig. 4. Conversion degree of *I vs.* time at temperature 60 °C, pressure 0.34 MPa, mass ratio of 0.6 % Pd/CaCO₃ to *I* 6.6 x 10⁻³ and various mole ratios of KOH to Pd: *1.* 0.39 x 10², *2.* 0.77 x 10², *3.* 1.20 x 10², *4.* 1.58 x 10², *5.* 1.96 x 10².
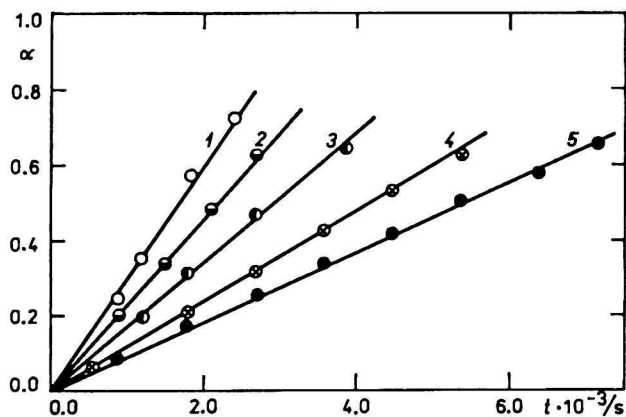
Fig. 5. Conversion degree of I vs. time at pressure 0.34 MPa, mass ratio of 0.6 % $Pd/CaCO_3$ to I 6.6×10^{-3}, mole ratio of KOH to Pd 1.58×10^2 and various temperatures/°C: *1*. 60, *2*. 50, *3*. 40, *4*. 30, *5*. 22.
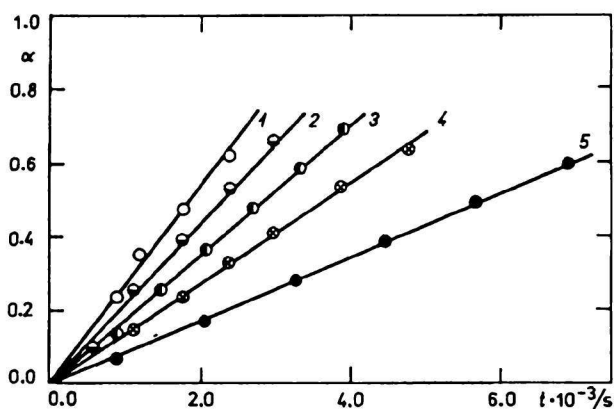

Fig. 6. Conversion degree of I vs. time at temperature 60 °C, mass ratio of 0.6 % $Pd/CaCO_3$ to I 6.6×10^{-3} and mole ratio of KOH to Pd 1.58×10^2 and various pressures/MPa: *1*. 0.34, *2*. 0.30, *3*. 0.25, *4*. 0.20, *5*. 0.15.
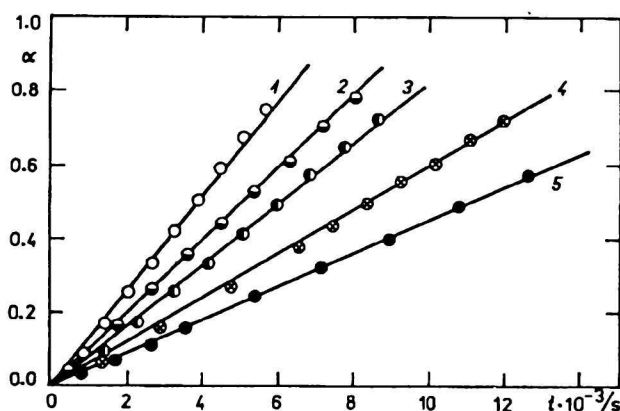

Fig. 7. Conversion degree of I vs. time at pressure 0.34 MPa, mass ratio of 6.0 % $Pd/CaCO_3$ to I 1.1×10^{-3} and mole ratio of KOH to Pd 0.48×10^2 and various temperatures/°C: *1*. 60, *2*. 50, *3*. 40, *4*. 30, *5*. 22.

Time dependence of concentrations of I is linear and transformation rate of I is controlled by the rate equation of zero-order reactions. Rate constants were calculated from the determined concentration relationships. The overall selectivity of hydrogenation is understood as the ratio of masses of the required product II and consumed starting compound I (Tables 1 and 2). Influence of various catalysts and bases on the reaction rate and total selectivity of catalytic hydrogenation are presented in Table 3.

Catalytic hydrogenations of I with palladium supported on calcium carbonate in the absence of base did not stop after consumption of one hydrogen equivalent and yielded saturated hydrogenation product III (Scheme 1). By halting the hydrogenation manually at the end of the first stage at 60 °C under pressure 0.34 MPa, compound II can be obtained with 90.5—94.5 % selectivity. Increasing the mass ratio of catalyst to I effected an increase of reaction rate and decrease of selectivity.

Catalytic hydrogenations with palladium supported on calcium carbonate in the presence of base stopped spontaneously close to consumption of one hydrogen equivalent, yielded parallel II, III and selectivity of the formation of II was 91.2—98.1 %. The presence of weak bases (quinoline, pyridinium N-oxide) did not cause great changes in the reaction rate and selectivity, the presence of strong bases (sodium methoxide, potassium hydroxide) caused a significant decrease of the reaction rate and increase of selectivity.

Table 1. Calculated Rate Constants and Selectivity of Catalytic Hydrogenation of I Using 0.6 % $Pd/CaCO_3$ in the Presence of KOH

m(Catalyst)/ $/m(I)$	n(Base)/ $/n$(Pd)	θ	p	$k \cdot 10^4$	Selectivity
10^{-3}	10^2	°C	MPa	kmol m^{-3} s^{-1}	%
8.2	0	60	0.34	21.89 ± 0.5	92.0
6.6	0	60	0.34	18.81 ± 0.17	93.0
4.9	0	60	0.34	14.93 ± 0.22	93.2
3.3	0	60	0.34	11.06 ± 0.16	93.6
1.6	0	60	0.34	7.03 ± 0.06	94.5
6.6	0.39	60	0.34	15.09 ± 0.34	94.0
6.6	0.77	60	0.34	13.69 ± 0.38	96.0
6.6	1.20	60	0.34	11.84 ± 0.29	97.6
6.6	1.58	60	0.34	9.24 ± 0.43	98.0
6.6	1.96	60	0.34	8.11 ± 0.64	98.0
6.6	1.58	50	0.34	7.08 ± 0.08	97.8
6.6	1.58	40	0.34	5.22 ± 0.06	98.0
6.6	1.58	30	0.34	3.64 ± 0.02	98.0
6.6	1.58	20	0.34	2.88 ± 0.02	97.7
6.6	1.58	60	0.30	7.93 ± 0.34	98.0
6.6	1.58	60	0.25	6.84 ± 0.04	98.0
6.6	1.58	60	0.20	5.50 ± 0.04	97.9
6.6	1.58	60	0.15	2.76 ± 0.01	98.0

Table 2. Calculated Rate Constants and Selectivity of Catalytic Hydrogenation of *I* Using 6 % Pd/CaCO₃ in the Presence of KOH at Pressure 0.34 MPa

m(Catalyst) : $m(I)$	n(Base) : n(Pd)	θ	$k \cdot 10^4$	Selectivity
10^{-3}	10^2	°C	kmol m⁻³ s⁻¹	%
1.1	0	60	7.96 ± 0.28	91.0
1.1	0.12	60	6.69 ± 0.12	93.8
1.1	0.24	60	5.23 ± 0.07	95.9
1.1	0.48	60	4.04 ± 0.05	96.2
1.1	0.60	60	3.81 ± 0.09	96.3
1.1	0.48	50	3.05 ± 0.03	96.5
1.1	0.48	40	2.56 ± 0.03	96.8
1.1	0.48	30	1.84 ± 0.02	96.9
1.1	0.48	22	1.41 ± 0.01	96.7

Table 3. Calculated Rate Constants and Selectivity of Catalytic Hydrogenation of *I* at Temperature 60 °C and Pressure 0.34 MPa

Catalyst[a]	m(Catalyst)/ $/m(I)$	Base[b]	n(Base)/ $/n$(Pd)	$k \cdot 10^4$	Selectivity
	10^{-3}		10^2	kmol m⁻³ s⁻¹	%
K₁	6.6	–	0	18.81 ± 0.17	93.0
K₁	6.6	B₁	1.86	17.61 ± 0.08	93.8
K₁	6.6	B₂	1.37	17.36 ± 0.49	94.7
K₁	6.6	B₃	1.63	10.03 ± 0.10	97.6
K₁	6.6	B₄	1.58	9.25 ± 0.43	98.0
K₂	1.1	–	0	7.96 ± 0.28	91.0
K₂	1.1	B₁	1.17	6.70 ± 0.12	93.4
K₂	1.1	B₂	1.13	6.35 ± 0.15	93.7
K₂	1.1	B₃	0.66	3.13 ± 0.12	96.5
K₂	1.1	B₄	0.48	4.04 ± 0.14	96.2
K₃	6.6	–	0	11.89 ± 0.03	90.5
K₃	6.6	B₂	1.64	11.13 ± 0.04	91.2
K₃	6.6	B₁	1.97	9.23 ± 0.13	91.7
K₃	6.6	B₃	0.50	6.60 ± 0.16	95.6
K₃	6.6	B₄	0.57	5.33 ± 0.19	96.0
K₄	1.1	–	0	10.54 ± 0.21	92.0
K₄	1.1	B₂	1.08	9.62 ± 0.05	92.5
K₄	1.1	B₁	1.39	8.27 ± 0.19	95.7
K₄	1.1	B₃	0.59	6.31 ± 0.07	98.1
K₄	1.1	B₄	0.36	4.64 ± 0.20	97.8

a) K₁ - 0.6 % Pd/CaCO₃, K₂ - 6.0 % Pd/CaCO₃, K₃ - 0.5 % Pd + 0.5 % Pb/CaCO₃, K₄ - 5.0 % Pd + 5.0 % Pb/CaCO₃. *b)* B₁ - pyridinium *N*-oxide, B₂ - quinoline, B₃ - sodium methoxide, B₄ - potassium hydroxide.

The measured data served for calculation of the rate constants (Tables 1 and 2) for which, employing the Arrhenius equation, the values of activation energies $E = (22.3 \pm 1.0)$ kJ mol⁻¹ (6 % Pd/CaCO₃) and $E = (24.3 \pm 1.0)$ kJ mol⁻¹ (0.6 % Pd/CaCO₃) were determined.

In summary, participation of a base in hydrogenation of 3,7-dimethyl-6-octen-1-yn-3-ol using palladium on calcium carbonate catalysts resulted in inhibition of the consecutive reaction of the product 3,7-dimethyl-1,6-octadien-3-ol and in decrease of the rate of conversion of the starting compound into undesirable product.

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