CHEMISTRY LETTERS, pp. 167-170, 1987.

Phenylacetaldehyde as an Effective Additive for the Selective Hydrogenation of Some Nonconjugated Dienes to Monoenes over Palladium Catalysts

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Methyl linoleate and 1,5-cyclooctadiene are hydrogenated with high selectivity to the corresponding monoenes over palladium catalysts in the presence of added phenylacetaldehyde, with almost complete depression of the hydrogenation to the saturates.

Selective hydrogenation of polyenes to monoenes is an important application of hydrogenation catalysts in organic synthesis.[1)] Although high selectivity is usually obtained in the hydrogenation of conjugated dienes, selectivity tends to become lower with nonconjugated dienes,[2)] except with some homogeneous[3)] and colloidal catalysts.[4,5)]

During the studies on the selective hydrogenation of methyl linolenate with a palladium catalyst, it has been noticed that unpurified methyl linolenate is very selectively hydrogenated to methyl octadecenoates with practically no further hydrogenation to methyl stearate. Although we could not identify the effective principle in the unpurified material, it has been found that among various aldehydic compounds phenylacetaldehyde depresses almost completely the hydrogenation of methyl linoleate to the saturate as shown in Fig. 1. The addition of phenylacetaldehyde is also very effective for the selective hydrogenation of 1,5-cyclooctadiene to cyclooctene as shown in Fig. 2. In Tables 1 and 2 are summarized the effects of various additives on the hydrogenation of methyl linoleate and 1,5-cyclooctadiene, respectively. The selectivity is shown in terms of the ratio V_D/V_M where V_D is the rate of disappearance of a diene and V_M is the rate of disappearance of the monoene formed from the diene. Since hydrogenation of 1,5-cyclooctadiene is accompanied by the isomerization to 1,4-cyclooctadiene, V_D was obtained from the rate of formation of cyclooctene. The values of V_D/V_M shown in the Tables clearly indicate that phenylacetaldehyde is far more effective than any of the aldehydes investigated for both Pd-$CaCO_3$ and Pd black catalysts. Thus, in the presence of added phenylacetaldehyde the monoenes are formed in the maximum yields of 99.1% (Pd-$CaCO_3$) and 98.8% (Pd black) with methyl linoleate and in the yields of 97.6% (Pd-$CaCO_3$) and 97.4% (Pd black) with 1,5-cyclooctadiene in hydrogenation in THF at 25 °C and atmospheric pressure. The formation of saturate is of very low level even after 5 h reaction. High selectivity is also obtained in cyclohexane as solvent, but the use of t-butyl alcohol

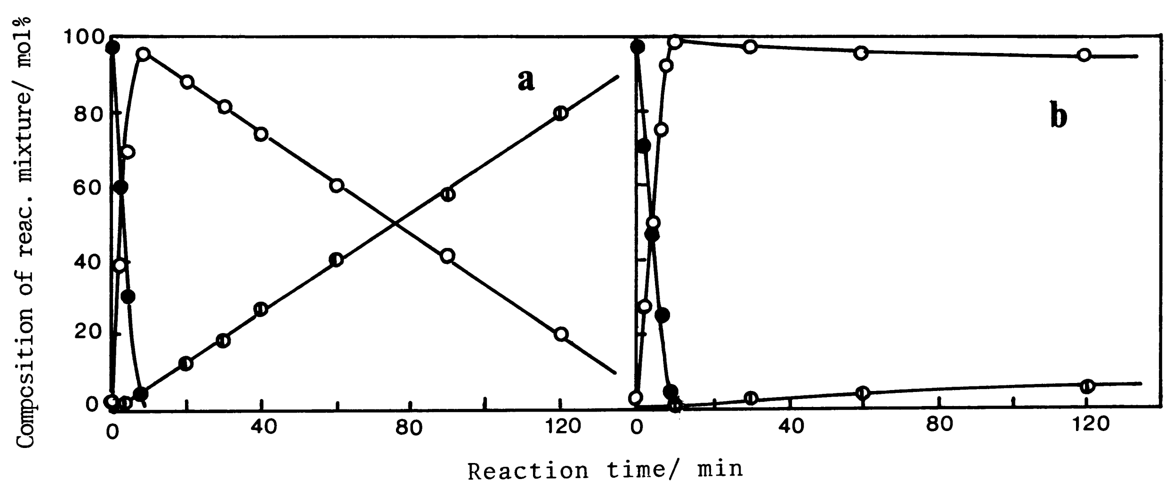

Fig. 1. Hydrogenation of methyl linoleate with 5% Pd-$CaCO_3$ in THF; (a): hydrogenation without additive, (b): hydrogenation with addition of $PhCH_2CHO$. For reaction conditions, see Table 1. (●): methyl linoleate, (○): methyl octadecenoate, and (⦶): methyl stearate.

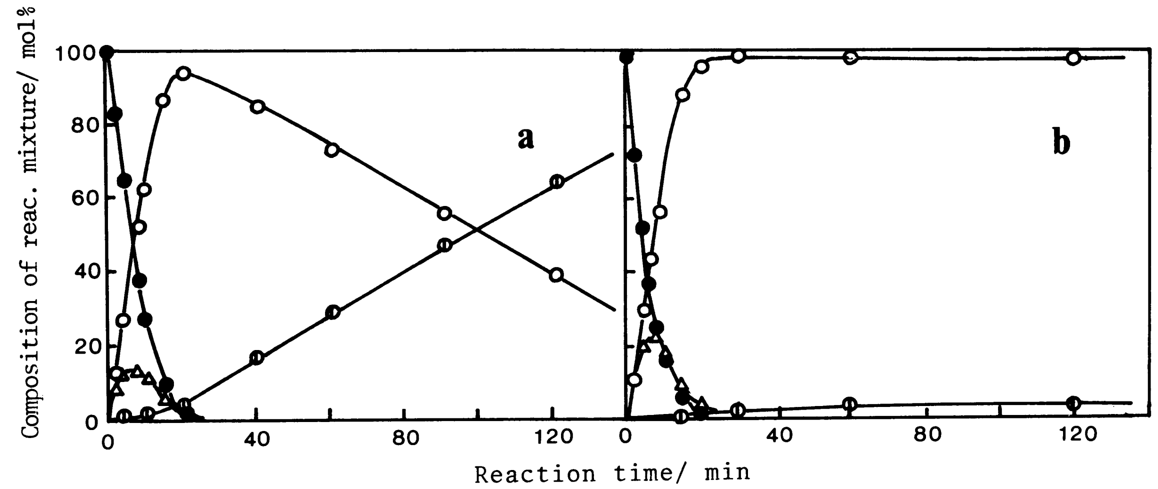

Fig. 2. Hydrogenation of 1,5-cyclooctadiene with Pd black in THF; (a): hydrogenation without additive, (b): hydrogenation with addition of $PhCH_2CHO$. For reaction conditions, see Table 2. (●): 1,5-cyclooctadiene, (△): 1,4-cyclooctadiene, (○): cyclooctene, and (⦶): cyclooctane.

lowers the effect of the aldehyde. The addition of quinoline which is known to be effective for the selective hydrogenation of alkynes$^{1)}$ and conjugated dienes$^{6)}$ greatly depressed the hydrogenation of the dienes as well as the monoenes, with the results of low values of V_D/V_M.

From individual and competitive hydrogenations, relative strengths of adsorption were estimated for the compounds investigated. The results are given in Table 3. It is seen that rather large differences exist between the adsorption coefficients of the dienes and the corresponding monoenes, which may explain rather high maximum yields of the monoenes even over unpoisoned catalysts. It is noted that 1,5-cyclooctadiene and cyclooctene are adsorbed more strongly than

Table 1. Hydrogenation of Methyl Linoleate a)

Catalyst	Solvent	Additive b)	10^2v_D c)	10^2v_M d)	v_D/v_M	C_M/% e)	
			mol min^{-1} $gmetal^{-1}$			at max.	after 5 h
5%Pd-$CaCO_3$	THF	-	16	0.66	25	95.4	0
5%Pd-$CaCO_3$	THF	Benzene	18	0.30	59	97.5	18.9
5%Pd-$CaCO_3$	THF	PhCHO	8.0	0.18	45	97.7	63.8
5%Pd-$CaCO_3$	THF	$PhCH_2CHO$	12	0.023	520	99.1	92.4
5%Pd-$CaCO_3$	THF	$Ph(CH_2)_2CHO$	14	0.26	56	97.9	29.8
5%Pd-$CaCO_3$	THF	$Ph(CH_2)_3CHO$	9.4	0.22	43	98.0	45.3
5%Pd-$CaCO_3$	THF	$CH_3(CH_2)_2CHO$	22	0.94	24	96.0	0
5%Pd-$CaCO_3$	C_6H_{12} f)	$PhCH_2CHO$	6.0	0	Very large	98.6	98.6
5%Pd-$CaCO_3$	t-BuOH	$PhCH_2CHO$	13.4	0.23	58	97.3	59.4
5%Pd-$CaCO_3$	THF	Quinoline	0.2	0.07	3	84.6	64.6
Pd black	THF	-	1.8	0.56	3	93.2	0
Pd black	THF	$PhCH_2CHO$	0.7	0.003	230	98.8	90.7

a) Methyl linoleate (3×10^{-4} mol) was hydrogenated with 6 mg of 5% Pd-$CaCO_3$ or 3 mg of Pd black as catalyst in 1.6 ml of solvent at 25 °C and atmospheric pressure. b) The additive (2×10^{-4} mol; 2×10^{-5} mol for quinoline) was added to prereduced catalyst before the addition of substrate. c) The rate of disappearance of methyl linoleate. d) The rate of disappearance of methyl octadecenoates. e) The concentration of octadecenoates in reaction mixture. f) Cyclohexane.

Table 2. Hydrogenation of 1,5-Cyclooctadiene a)

Catalyst	Additive b)	10^2v_D c)	10^2v_M d)	v_D/v_M	C_M/% e)		$C_{1,4}$/% f)
		mol min^{-1} $gmetal^{-1}$			at max.	after 5 h	at max.
5%Pd-$CaCO_3$	-	9.5	0.32	30	94.6	33.5	10.3
5%Pd-$CaCO_3$	Benzene	7.2	0.22	33	94.2	52.6	11.9
5%Pd-$CaCO_3$	$PhCH_2CHO$	8.9	0.014	645	97.6	95.4	19.5
5%Pd-$CaCO_3$	$Ph(CH_2)_2CHO$	7.9	0.24	33	96.6	47.5	15.0
5%Pd-$CaCO_3$	$Ph(CH_2)_3CHO$	7.2	0.19	38	96.5	60.7	17.7
5%Pd-$CaCO_3$	$CH_3(CH_2)_2CHO$	8.7	0.27	32	96.8	43.2	16.1
5%Pd-$CaCO_3$	Quinoline	0.2	0.02	10	76.6	76.6	6.4
Pd black	-	1.3	0.12	11	93.2	0	12.4
Pd black	$PhCH_2CHO$	1.3	0.0013	1000	97.4	93.6	20.9

a) 1,5-Cyclooctadiene (4×10^{-4} mol) was hydrogenated with 6 mg of 5% Pd-$CaCO_3$ or 2 mg of Pd black in 1.6 ml of THF at 25 °C and atmospheric pressure. b) See footnote b) in Table 1. c) The rate of formation of cyclooctene. d) The rate of disappearance of cyclooctene. e) The concentration of cyclooctene in reaction mixture. f) The concentration of 1,4-cyclooctadiene in reaction mixture at the maximum.

Table 3. Rates of Individual and Competitive Hydrogenations$^{a)}$

Compound$^{b)}$	$10^3V^{c)}$ mol min^{-1}gmetal^{-1}	Relative reactivity	Ratio of ads. coefficient$^{d)}$	Relative strength of ads.
Methyl oleate	4.0	0.32(MO/COE)	0.30(MO/COE)	1
Cyclooctene	3.7	0.013(COE/COD)$^{e)}$	0.073(COE/COD)	3.3
Methyl linoleate	17.8	0.37(ML/COD)	0.43(ML/COD)	19
1,5-Cyclooctadiene	20.9			45

a) The compound (5.4 x 10^{-4}mol) was hydrogenated individually or in an equimolar mixture with 2 mg of Pd black in 3.2 ml of THF at 50 °C and atmospheric pressure. b) Abbreviated to MO, COE, ML, and COD, respectively. c) Rate of individual hydrogenation. d) Obtained from the relationship of R(A/B) = V(A/B) x b(A/B) where R and b indicate the relative reactivity and adsorption coefficient of A to B, respectively. e) Evaluated from the maximum concentration of COE, $(C_{COE})_{max}$(= 0.943), in the hydrogenation of COD when the initial concentration of COD was taken as unity, using the relationship of $(C_{COE})_{max} = R^{R/(1-R)}$ where R is the relative reactivity of COE to COD[F.Coussemant and J. C. Jungers, Bull. Soc. Chim. Belg., 59, 295 (1950)].

methyl linoleate and methyl oleate, respectively. This is in line with the facts that, while phenylacetaldehyde depressed the V_D for methyl linoleate, it affects the V_D for 1,5-cyclooctadiene only slightly. From the results the strength of adsorption may be ordered as follows: 1,3-cyclooctadiene > (quinoline) >> 1,5-cycloctadiene > methyl linoleate > (phenylacetaldehyde) >> cyclooctene > methyl oleate.

With addition of phenylacetaldehyde isomerization of 1,5- to 1,4-cyclooctadiene during hydrogenation increases as seen in Table 2. This may also contribute to the observed high selectivity, especially in the case of methyl linoleate in which such isomerization may directly lead to the formation of a conjugated diene. It is further noted that the trans content of the octadecenoates formed from linoleate, as determined by the IR method,7) increased from 51.5% at 5.4% of the saturate over unpoisoned Pd-$CaCO_3$ to 58% at 1.0% of the saturate and 65.8% at 5.6% of the saturate over a phenylacetaldehyde poisond Pd-$CaCO_3$.

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(Received October 13, 1986)