View Article Online / Journal Homepage / Table of Contents for this issue

Published on 01 January 1981. Downloaded by University of Illinois at Chicago on 03/02/2014 10:58:06.

Active Metals from Potassium–Graphite. Palladium–Graphite as Catalyst in the Hydrogenation of Nitro-compounds, Alkenes, and Alkynes

By Diego Savoia, Claudio Trombini, Achille Umani-Ronchi, and Giancarlo Verardo
(*Istituto Chimico 'G. Ciamician,' via Selmi 2, Università di Bologna, Italy*)

Summary Palladium–graphite, prepared by reduction of $PdCl_2$ by means of C_8K in 1,2-dimethoxyethane, is an effective catalyst for the hydrogenation of aromatic nitro-compounds, alkenes, and alkynes to anilines, alkanes, and (*Z*)-alkenes, respectively.

We recently reported the reduction of transition metal salts dissolved in tetrahydrofuran with potassium–graphite (C_8K).[1] By this procedure highly dispersed nickel on graphite was obtained and used as hydrogenation catalyst.[2]

We now report the preparation of active palladium dispersed on the graphite surface (Pd–Gr)† according to equation (1) and the preliminary results obtained in hydrogenation reactions.[3]

$$2C_8K + PdCl_2 \rightarrow C_{16}Pd + 2KCl \qquad (1)$$

In a typical preparation, 1·77 g of palladium chloride (Ventron) and 40 ml of 1,2-dimethoxyethane (freshly distilled from sodium benzophenone ketyl) were added to a slurry of potassium–graphite, prepared[1] from 0·78 g of potassium and 1·97 g of graphite powder (Roth), in 10 ml of 1,2-dimethoxyethane. The mixture was stirred at 100 °C for 8 h (external oil-bath), then was cooled to room temperature, and 2 ml of water were added. The solid phase was filtered and washed with 20 ml of 0·1N HCl, 200 ml of hot water, 20 ml of methanol, 20 ml of ether, and was finally dried *in vacuo* (0·01 mmHg) at 80 °C. Palladium content by weight in samples obtained from three different preparations was 33 ± 2% ($C_{16}Pd$ requires 35% of Pd).

The activity of this new catalyst was first investigated for the hydrogenation of oct-2-ene, 3-methylnitrobenzene, 4-methoxynitrobenzene, and 4-nitrobenzoic acid, which were quantitatively converted into octane, 3-methylaminobenzene, 4-methoxyaminobenzene, and 4-aminobenzoic acid in methanol at room temperature and atmospheric pressure.‡ These results indicate that Pd–Gr can provide an alternative to the commonly used palladium on carbon.[4]

Table. Pd–Gr-catalysed semihydrogenation of alkynes.[a]

Run	Alkyne	Alkane (%)[b]	Alkene (%)[b]	*Z*/*E* ratio[b]
1	Dec-1-yne[c]	6	90	
2	Dec-1-yne	2	95	
3	Hex-1-yn-3-ol	3	94	
4	Ethyl phenylpropynoate[c]	29	44	89·1/10·9
5	Ethyl phenylpropynoate	3	92[d]	97·8/2·2
6	Diphenylacetylene	2	97[e]	94·0/6·0
7	Dec-5-yne	< 1	99	98·1/1·9[f]
8	Dec-5-yne[g]	4	93	93·6/6·4[f]

[a] Typical quantities: alkyne (5 mmol), MeOH (5 ml), EDA (0·3 ml), and Pd–Gr (50 mg, corresponding to *ca.* 3 mol % of Pd). Hydrogenations were carried out at 20 ± 3 °C and under atmospheric pressure, with stirring at 1100 r.p.m. Hydrogen uptake ranged between 3 ml/min (run 1) and 11 ml/min (run 6). After absorption of 1 equiv. of hydrogen, the uptake rate decreased to about 50% of the previous value in the absence of EDA, while in the presence of EDA, a very sharp end-point was observed, the hydrogen uptake falling to 0·3—0·5 ml/min (runs 2, 3, 5, and 6) or ceasing as in the case of dec-5-yne (run 7). [b] Values based on g.l.c. analysis (2m × 0·25 in column packed with 15% Carbowax 20M on Chromosorb W 80—100 mesh) after consumption of 5 mmol of hydrogen. All compounds gave satisfactory i.r., ^1H n.m.r., and mass spectra. In particular, i.r. spectra of disubstituted alkenes showed only very weak bands at 960 cm^{-1}. [c] Runs carried out in the absence of EDA. [d] ^1H N.m.r. δ ($CDCl_3$, Me_4Si) 7·2—7·8 (m, 5H), 6·85 (d, 1H, *J* 12·7 Hz), 5·85 (d, 1H, *J* 12·7 Hz), 4·1 (q, 2H), and 1·2 (t, 3H). [e] ^1H N.m.r. δ (CCl_4, Me_4Si) 7·2 (s, 10H) and 6·55 (s, 2H). [f] Value determined by the g.l.c. peak area ratio of the diastereomeric epoxides obtained by treatment of the hydrogenated mixture with 3-chloroperbenzoic acid in CH_2Cl_2 at 0 °C. [g] Pd–Gr is replaced by 10% palladium on carbon (Aldrich, 60 mg).

Moreover, Pd–Gr has been found to be an effective catalyst in the semihydrogenation of mono- and disubstituted alkynes (Table). It is apparent from runs 1 and 4 that, after absorption of 1 equiv. of hydrogen, alkenes were produced with unsatisfactory stereospecificity and accompanied by not negligible amounts of fully hydrogenated compounds. However the catalyst performances were

---

† The *X*-ray diffraction spectrum (Debye–Scherrer camera) of Pd–Gr showed both graphite and palladium reflections.

‡ Hydrogenation reactions were carried out on a 5 mmol scale of substrate in 5 ml of MeOH at 20 ± 3 °C using 50 mg of Pd–Gr (*ca.* 3 mol % of Pd).

View Article Online

markedly improved by addition of ethylenediamine (EDA), as is shown by runs 2, 3, 5, 6, and 7. In fact, full hydrogenation was almost completely suppressed and (Z)-alkenes were obtained with a stereospecificity comparable with or superior to that exhibited by Lindlar[5] or nickel P-2[6] catalysts.

For a direct comparison, we hydrogenated dec-5-yne using 10% palladium on carbon (Aldrich) in the presence of EDA (run 8), under the same experimental conditions used in run 7. Although the hydrogenation rate (14 ml/min) was higher than in the case of palladium–graphite (7·2 ml/min), probably owing to different metal surface areas owing to the different support, metal content, and preparation procedure,[7] the alkene–alkane ratio and the stereospecificity were considerably lower.

(*Received*, 23*rd March* 1981; *Com.* 327.)

---

[1] D. Braga, A. Ripamonti, D. Savoia, C. Trombini, and A. Umani-Ronchi, *J. Chem. Soc., Chem. Commun.*, 1978, 927; *J. Chem. Soc., Dalton Trans.*, 1979, 2026.

[2] D. Savoia, E. Tagliavini, C. Trombini, and A. Umani-Ronchi, unpublished results.

[3] For palladium catalysts in heterogeneous hydrogenations, see P. N. Rylander, 'Catalytic Hydrogenation in Organic Syntheses,' Academic Press, New York, 1979. For the use of polymer-bound palladium catalysts in the hydrogenation of alkynes, see M. Terasawa, H. Yamamoto, K. Kaneda, T. Imanaka, and S. Teranishi, *J. Catal.*, 1979, **57**, 315; R. J. Card, C. E. Liesner, and D. C. Neckers, *J. Org. Chem.*, 1979, **44**, 1095; N. L. Holy and S. R. Shelton, *Tetrahedron*, 1981, **37**, 25. For palladium on carbon-catalysed triethylammonium formate reduction of alkynes and aromatic nitro-compounds, see J. R. Weir, B. A. Patel, and R. F. Heck, *J. Org. Chem.*, 1980, **45**, 4926; M. O. Terpko and R. F. Heck, *ibid.*, p. 4993.

[4] P. M. Rylander, 'Catalytic Hydrogenation in Organic Syntheses,' Academic Press, New York, 1979, chs. 3 and 7.

[5] E. N. Marvell and T. Li, *Synthesis*, 1973, 457.

[6] C. A. Brown and V. K. Ahuja, *J. Org. Chem.*, 1973, **38**, 2226; *J. Chem. Soc., Chem. Commun.*, 1973, 553; R. G. Smith, G. D. Daves, Jr., and G. E. Daterman, *J. Org. Chem.*, 1975, **40**, 1593.

[7] P. Mozingo, *Org. Synth.*, 1946, **26**, 78.

Published on 01 January 1981. Downloaded by University of Illinois at Chicago on 03/02/2014 10:58:06.