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Platinum-Catalysed Hydrogenolysis of Phenol to Benzene

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Abstract

Benzene is obtained during reduction of phenol by hydrogen in the presence of platinum black under mild conditions.

Introduction

Benzene was formed during electrochemical reduction of phenol at a platinum black electrode in dilute acid at room temperature.[1] According to a standard text,[2] 'loss of oxygen without some reduction of the aromatic ring is rarely observed in catalytic hydrogenation of phenols and phenyl ethers under mild conditions'.

Generation of benzene could have been the result of a difference in mechanism between electrochemical reduction and chemical reduction of phenol. However, our previous conclusions and those of others[3] were that both chemical and electrochemical reduction proceed by similar schemes. In our experiments[1] the benzene was continuously removed by purging with nitrogen gas. This suggests that we observe benzene because it is removed from the reaction centre before it can be reduced to cyclohexane. Others have not detected benzene because their reductions were carried to completion in closed vessels. In order to test this hypothesis we have examined chemical reduction of phenol with hydrogen in the presence of platinum black under conditions as similar as possible to the previous electrochemical studies.

Experimental

Instruments and methods of analysing vapour and liquid samples have been described previously.[1] The following is a typical experiment.

Phenol (10·8 mmol) in 1 M sulfuric acid (250 ml) was stirred in a round-bottomed flask immersed in a constant temperature (24·8°C) bath. A platinum black strip (2·5 by 3·0 cm), which had been used previously[1] as an electrode, was suspended in the solution and hydrogen continuously bubbled (24·5 ± 0·5 ml min^{-1}) close to its surface. All vapours carried over by the hydrogen were collected in a dry-ice/acetone cold-trap. The amounts of benzene and cyclohexane in vapour samples (0·5 ml, removed before the cold-trap) and phenol, cyclohexanone and cyclohexanol in small samples of the reaction solution were monitored by gas chromatography as described previously.[1] After 30 h the

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[1] Bagnell, L. J., and Jeffery, E. A., *Aust. J. Chem.*, 1980, **33**, 2565.

[2] Rylander, P. N., 'Catalytic Hydrogenation over Platinum Metals' p. 334 (Academic Press: London 1967).

[3] Miller, L. L., and Christensen, L., *J. Org. Chem.*, 1978, **43**, 2059.

reduction was stopped and the final amounts of benzene and cyclohexane were confirmed from the contents of the cold-trap. Found: benzene (0·50 mmol), cyclohexane (0·66 mmol), cyclohexanone (1·02 mmol), cyclohexanol (0·022 mmol) and phenol (8·5 mmol).

Results and Discussions

The percentages of benzene, cyclohexane and cyclohexanone plus cyclohexanol, obtained after *c.* 20% of the phenol had been reduced, are shown in Table 1.

Raising the temperature increased the yield of benzene (runs 1–3). Cyclohexanol or cyclohexanone, when present initially in one-fifth of the phenol concentration, had no marked effect upon the product distribution (runs 4 and 5). The slightly higher yield of cyclohexane in run 5 is probably caused by reduction of some of the cyclohexanone to cyclohexane and cyclohexanol; a process confirmed by a separate experiment. Carrying out the reaction in 1 M hydrochloric acid, rather than 1 M sulfuric acid, did not grossly alter the product distribution (run 6). These chemical reductions can be simulated by electrochemical reduction[1] at very low current densities (run 7).

Table 1. Catalytic hydrogenation of phenol with hydrogen at atmospheric pressure in 1 M sulfuric acid

Run No.	Bath temp. (°C)	Reaction time (h)	Products after 20±2% conversion (%)		
			Benzene	Cyclohexane	Cyclohexanone+cyclohexanol
1	24·8	30·0	25·8	28·2	46·0
2	50·5	16·0	66·4	11·4	21·9
3	80·5	9·0	87·3	3·1	9·5
4[A]	24·8	30·0	19·2	32·5	48·3
5[B]	24·8	30·0	21·9	42·2	36·6
6[C]	24·8	26·5	32·1	31·6	38·6
7[C,D]	24·8	26·5	33·6	36·5	29·9

[A] Substrate was phenol (0·043 M) and cyclohexanol (0·0087 M). [B] Substrate was phenol (0·043 M) and cyclohexanone (0·010 M). [C] In 1 M hydrochloric acid. [D] Electrochemical reduction.

Raising the current density decreases the ratio of benzene to cyclohexane. Indeed, our previous electrochemical studies with higher current densities[1] gave much less benzene. A slow reduction should allow time for the benzene to diffuse from the catalyst surface and to be purged from the reaction vessel. Cyclohexane should be formed if there is not enough time for the intermediate benzene to diffuse away from the catalyst.

Such a simple explanation, however, conflicts with the higher yield of benzene at the higher temperatures, where the rate of reduction was faster. Benzene should be purged from the reaction vessel more efficiently at the higher temperatures and this could offset the faster rate of reduction.

Lastly, decomposition of other products is not a source of benzene. Under our catalytic reducing conditions at 80·5°C cyclohexanol slowly decomposes (0·2% per hour) to cyclohexane (80%) and cyclohexene (20%); cyclohexanone decomposes (1·5% per hour) to cyclohexanol (66%), cyclohexane (34%) and traces of benzene (0·3–0·4%). Furthermore, these experiments indicate that cyclohexane does not dehydrogenate during the reactions.

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