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A new advanced method for heterogeneous catalysed dechlorination of 1,2,3-, 1,2,4-, and 1,3,5-trichlorobenzenes in hydrocarbon solvent

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Abstract—A new advanced method for dechlorination of 1,2,3-, 1,2,4-, and 1,3,5-trichlorobenzenes in organic solvent catalysed by palladium on carbon support and solid hydrazine hydrochloride yields benzene in short reaction times. The catalyst system can be efficiently reused for several cycles. Ultrasound radiation of the heterogeneous catalyst reaction increases remarkably the rate of dechlorination. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

Chlorinated organic molecules, especially aromatic compounds, present a very important environmental problem because they are extremely persistent due to their slow biodegradation, their toxicity and carcinogenic character have been widely proved.[1] The combustion of chlorinated compounds releases even more toxic compounds such as polychlorinated dibenzodioxins and polychlorinated dibenzofurans.[2]

In recent years, catalytic dechlorination methods have been developed including transfer hydrogenation by means of hydrogen donors such as metal hydrides,[3] formic acid and its salts[4] and alcohols,[5] which use water or methanol as solvents. The practical application of catalysts to the dechlorination of organic halides is always accompanied by the problem of the deactivation of the catalyst.[6]

We report here the first finding of a complete dechlorination of trichlorobenzenes in solution in hexane catalysed by palladium over carbon and hydrazine as hydrogen donor, at 60°C or room temperature and ultrasound source. Application of this methodology to the dechlorination of PCBs is in preparation and will be promptly presented.

2. Results and discussion

The samples of trichlorobenzenes (TCBs, 0.05 mmol) prepared for dechlorination were dissolved in hexane (40 g) and were treated with hydrazine hydrochloride (moderate toxic reagent[7]) (250 mg, 3.65 mmol) and sodium carbonate (390 mg, 3.65 mmol) and palladium on carbon (60 mg, Pd 10%, 0.056 mmol). A multi-frequency apparatus and ultrasonic reactors have been designed (with frequencies centered at 250, 475, 650 and 800 kHz) to improve the heterogeneous catalytic dechlorination. The reaction was run in a bath with stirring at variable temperature or in a reactor with ultrasonic radiation at room temperature, finally yielding benzene as the sole aromatic product (HPLC). The dechlorination reaction at 60°C (external bath) shows the highest kinetic. Moreover, ultrasonic irradiation produces a remarkable efficiency of the reaction in all of the frequencies experimented. However, the reaction completely proceeds for some shortest times, for 487 kHz versus 250 and 650 kHz.

The analysis of all the reaction products were carried out by HPLC with UV–vis detector, with an error <0.1%. Evaluated dichlorobenzenes (DCBs) and monochlorobenzene (MCB) hexane solutions were used as reference.

3. Dechlorination of the trichlorobenzenes

The results of the dechlorination of 1,2,3-; 1,2,4-; and 1,3,5-trichlorobenzene (1,2,3-; 1,2,4-; 1,3,5-TCB) under

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the above conditions are summarised in Table 1 (Scheme 1).

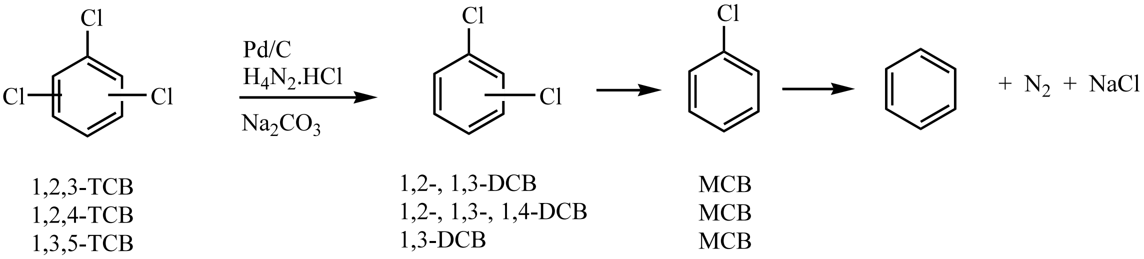
The reaction occasionally shows an initiation period but, after 5–10 min, yields sequentially the DCBs, MCB and benzene, in short reaction times. Ultrasonic irradiation avoids the initiation period. Moreover, some aspects of the reaction must be considered: (a) at 60°C the relative order of dechlorination of the TCB isomers was 1,2,3->1,3,5->1,2,4-TCB (Table 1). The temperature of the reaction (at rt or 40°C) does not modify the dechlorination order sequence. (b) In the same way, 1,3,5-TCB was transformed only in 1,3-DCB and benzene but MCB was not detected. (c) The 1,2,4-TCB allows a mixture of DCB isomers and MCB as chlorinated intermediates, being the 1,3-DCB isomer proportionally very abundant in the mixture. Hence, a *meta-rule*, meaning that Cl-atoms in the *meta* position would be removed preferentially, was not observed.[8] (d) Moreover, catalytic hydrogenation of the benzene ring

Table 1. Dechlorination of the TCBs

t (min)[a]	1,2,3-TCB	1,2+1,4-DCB	1,3-DCB	MCB	Benzene
15	0	0	0	0	100
5[b]	0	0	0	0	100
	1,2,4-TCB				
15	42	13	7	6	32
30	14	4	0	0	82
45	0	0	0	0	100
15[b]	0	0	0	0	100
	1,3,5-TCB				
15	0	–	26	0	74
30	0	–	0	0	100
10[b]	0	–	0	0	100

[a] At 60°C.

[b] Ultrasonic radiation (487 kHz).



Scheme 1.

Table 2. Dechlorination of the TCB with the recovered catalyst system

t (min)[a]	1,2,3-TCB	1,2+1,4-DCB	1,3-DCB	MCB	Benzene
15	46	18	0	8	28
30	29	22	0	12	37
45	0	0	0	0	100
30[b]	0	0	0	0	100
	1,2,4-TCB				
5	48	19	10	4	19
30	20	14	8	8	51
120	0	9	0	0	91
180	0	0	0	0	100
45[b]	0	0	0	0	100
	1,3,5-TCB				
15	22	–	19	6	53
30	10	–	11	0	79
45	0	–	5	0	95
60	0	–	0	0	100
30[b]	0	–	0	0	100

[a] At 60°C.

[b] Ultrasonic radiation (487 kHz).

was not detected. (e) In all cases, optimal sonication for TCBs dechlorination was obtained at 487 kHz, with the reaction time (Table 1).

After the first catalytic cycle, the palladium, hydrazine, sodium carbonate and sodium chloride were recovered by filtration on sodium carbonate and reused in the dechlorination of a new TCB solution problem. Incorporation of hydrazine hydrochloride was necessary to complete the reaction. The results are summarised in Table 2.

Although, in general, the recovered catalyst system exhibits a lowest efficiency at 60°C (external bath), the kinetics of dechlorination shows the same order observed in the first catalytic cycle, 1,2,3->1,3,5->1,2,4-TCB (Table 2). Moreover, the 1,2,3-TCB gives the 1,2-DCB dechlorination product, while 1,3,5-TCB gives 1,3-DCB and MCB was only observed at short reaction times. However, dechlorination of 1,2,4-TCB shows a mixture of DCB isomers, the 1,3-DCB proportionally being the main product and hence, the *meta rule* again fails. Dechlorination of TCBs in the second catalytic cycle shows the highest efficiency by ultrasonic radiation of the reaction at 487 kHz, at room temperature (Table 2).

Mono- and dichlorobenzenes separately show the same behaviour observed in the mixture.

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References

1. (a) Myneni, S. C. B. *Science* **2002**, *295*, 1039; (b) Fensterheim, R. J. *NLGI Spokesman* **2001**, *65*, 18; (c) Lin, C.-T. *Prog. Org. Coat.* **2001**, *42*, 226.
2. (a) Katami, T.; Yasuhara, A.; Okuda, T.; Shibamoto, T. *Environ. Sic. Technol.* **2002**, *36*, 1320; (b) Lemieux, P. M.; Lee, C. W.; Ryan, J. V.; Lutes, C. C. *Waste Manage.* **2001**, *21*, 419; (c) Lemieux, P. M.; Lee, C. W.; Ryan, J. V. *J. Air Waste Manage. Assoc.* **2000**, *50*, 2129; (d) Gullet, B. K.; Sarofim, A. F.; Smith, K. A.; Procaccini, C. *Process Saf. Environ. Prot.* **2000**, *78*, 47.
3. (a) Imamura, H.; Noda, Y.; Sakata, Y.; Tsuchiya, S. *J. Alloys Compd.* **2001**, *323–324*, 601; (b) Imamura, H.; Tanaka, T.; Sakata, Y.; Tsuchiya, S. *Catal. Lett.* **1998**, *56*, 65.
4. (a) Gowda, D. G. *Indian J. Chem.*, *Sect. B* **2002**, *41B*, 1064; (b) Yu, J.; Spencer, J. B. *Chemistry—A Eur. J.* **1999**, *5*, 2237; (c) Yu, J.; Spencer, J. B. *Chem. Commun.* **1998**, *18*, 1935; (d) Mizugaki, T.; Kanayama, Y.; Ebitani, K.; Kaneda, K. *J. Org. Chem.* **1998**, *63*, 2378.
5. Cho, Ch. S.; Kim, B. T.; Kim, T.-J.; Shim, S. Ch. *J. Org. Chem.* **2001**, *66*, 9020.
6. (a) Frankel, K. A.; Jang, B. W.-L.; Roberts, G. W.; Spivey, J. J. *Appl. Catal. A: General* **2001**, *209*, 401; (b) Frankel, K. A.; Jang, B. W.-L.; Spivey, J. J.; Roberts, G. W. *Appl. Catal. A: General* **2001**, *205*, 263; (c) Ordoñez, S.; Diez, F. W.; Sastre, H. *Appl. Catal. B: Environ.* **2001**, *31*, 113; (d) Choi, Y. H.; Lee, W. Y. *Catal. Lett.* **2000**, *67*, 155; (e) Heinrichs, B.; Noville, F.; Schoebrechts, J.-P.; Pirard, J.-P. *Stud. Surf. Sci. Catal.* **1999**, *126*, 443; (f) Chang, Ch.; Reo, C. M.; Lund, C. R. F. *Appl. Catal. B: Environ.* **1999**, *20*, 309.
7. Toch, B.; Erickson, J. *Toxicology* **1977**, *3*, 31.
8. Lassová, L.; Lee, H. K.; Hor, T. S. A. *J. Org. Chem.* **1998**, *63*, 3538.