

Catalytic dechlorination of chlorobenzenes: effect of solvent on efficiency and selectivity

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Abstract

Polychlorinated benzenes were dechlorinated with NaBH_4 , using $\text{PdCl}_2(\text{dppf})$ ($\text{dppf} = 1,1'$ -bis(diphenylphosphino)ferrocene) as the catalyst. A variety of solvents, namely THF, CH_3CN , DMSO, diglyme, DMF and DMA (dimethylacetamide) were examined. A supporting base, TMEDA (N,N,N,N -tetramethyl-1,2-ethylenediamine) was used in some cases. Catalytic activity was strongly solvent-dependent with DMA and DMF showing the best performance. Addition of TMEDA improved the yields in all cases, except for DMSO. In DMA, when TMEDA was used, the catalyst showed appreciable activity even after 2 weeks of reaction. Both solvent and the presence/absence of a base had a strong influence on the selectivity of the reaction. For example, the dechlorination of pentachlorobenzene led to 90% 1,2,3,4-tetrachlorobenzene in DMA/TMEDA, but to 80% 1,2,4,5-tetrachlorobenzene in DMSO/TMEDA. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Earlier, we reported [1] a catalytic system whereby chlorobenzenes and Aroclors are dechlorinated using $\text{PdCl}_2(\text{dppf})$ ($\text{dppf} = 1,1'$ -bis(diphenylphosphino)ferrocene) as catalyst, NaBH_4 as reducing agent, TMEDA (N,N,N,N -tetramethyl-1,2-ethylenediamine) as supporting base and THF as solvent. Preliminary tests suggested that by changing the solvent we could dramatically alter the behavior of the system.

This prompted us to study this phenomenon in detail. We herein explore the solvent effects using acetonitrile, DMSO, diglyme (diethylene glycol dimethyl ether), DMF (dimethylformamide), DMA (dimethylacetamide) and THF. The solvents chosen are able to dissolve the substrates and are inert towards NaBH_4 .

The substrates used in this study were pentachlorobenzene (C_6HCl_5), 1,2,3,4-tetrachlorobenzene ($1,2,3,4\text{-C}_6\text{H}_2\text{Cl}_4$), 1,2,3,5-tetrachlorobenzene ($1,2,3,5\text{-C}_6\text{H}_2\text{Cl}_4$), 1,2,3-trichlorobenzene ($1,2,3\text{-C}_6\text{H}_3\text{Cl}_3$) and 1,2,4-trichlorobenzene ($1,2,4\text{-C}_6\text{H}_3\text{Cl}_3$). These chlorinated benzenes provide a basis for selectivity studies,

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since the first dechlorination step can yield at least two isomers. For comparison of performance and selectivity, all reactions were repeated without the addition of TMEDA.

Selectivity in our case is defined as the ratio of isomeric products formed after the first dechlorination step. Readings were taken at the time when the concentration of the main product was highest. This is significant, as we are dealing with a non-equilibrium situation and the ratio of products does not remain constant over time¹. Other authors have reported selectivity for dechlorination reactions [2–5], but direct comparisons of our results with the literature data are not straightforward because the reported readings are usually taken at arbitrary intervals or only for one point in time.

Zhang et al. [2] reported the dechlorination of 1,2,4- $C_6H_3Cl_3$ in EtOH, leading to 70% 1,2-, 20% 1,3- and 10% 1,4- $C_6H_4Cl_2$. Marques et al. [3] performed the dechlorination of 1,2,4,5- $C_6H_2Cl_4$ in THF, which yields 1,2,4-trichlorobenzene and subsequently 90% *ortho* and 10% *para* $C_6H_4Cl_2$. In a more recent paper [4], these researchers reported that dechlorination of 1,2,4- $C_6H_3Cl_3$ in isooctane or ether gives 1,2-, 1,3- and 1,4- $C_6H_4Cl_2$ in the range of 50:20:30. Stiles [5] observed that 1,2,3,4- $C_6H_2Cl_4$ leads to 90% 1,2,4- and 10% 1,2,3- $C_6H_3Cl_3$ in ethanol/acetonitrile (6:1) and 1,2,4- $C_6H_3Cl_3$ gives 5% 1,2-, 20% 1,3- and 75% 1,4-dichlorobenzene in ethanol/acetonitrile (4:1). In ethanol/water (4:1), 1,2,3- $C_6H_3Cl_3$ decomposes to equal amounts of 1,2,3- and 1,2,4- $C_6H_3Cl_3$. A radical mechanism was proposed for this reaction. Apart from this, Tungler et al. [6] have found that a change in solvent influences the chemoselectivity (but not the regio-

¹ Consider for example the hypothetical decomposition of molecule A into two isomers B and C, which themselves give rise to species D. Only if the rate constants for forming B and C are identical and so are their decomposition rate constants, will the ratio of B and C remain constant over time.

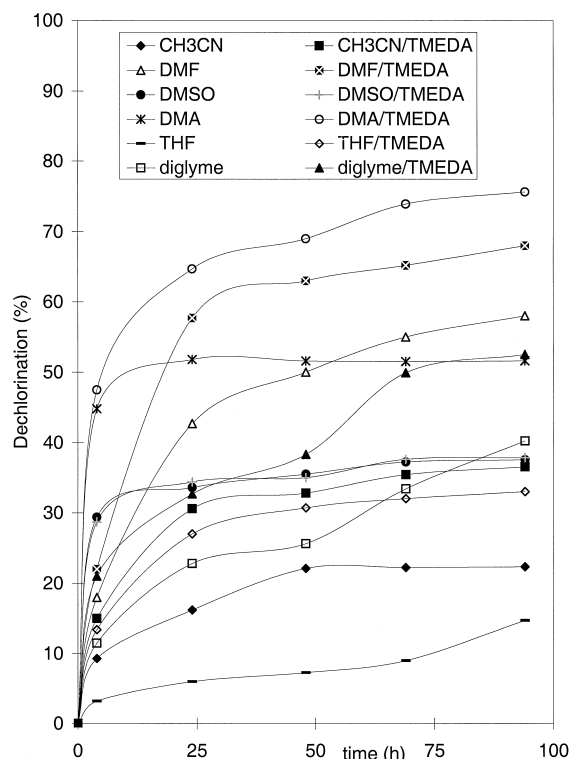


Fig. 1. Dechlorination of pentachlorobenzene in different solvents with and without TMEDA.

lectivity, as in the present case) of certain hydrogenation reactions.

2. Results and discussion

2.1. Performance

Fig. 1 shows the effect of different solvents on the dechlorination of C_6HCl_5 . DMA and DMF are the best solvents regardless of the presence of TMEDA. The use of these solvents leads to a ~70% dechlorination². Without TMEDA (a base), the reaction in DMA is fast,

² The dechlorination efficiency is expressed in terms of summation of the percent yields of the (partially) dechlorinated products, proportionated by the degree of chlorination. A 100% dechlorination in this context would refer to a 100% yield of benzene.

but the catalyst loses its activity after ~ 1 day. When TMEDA is added, the catalyst remains active even after ~ 100 h. For the other solvents, the efficiency decreases in the order of diglyme $>$ DMSO $>$ CH₃CN $>$ THF. Addition of the base improves the performance in all cases, except when DMSO is used. This is most evident in the case of THF, where dechlorination efficiency rises from 7% to 31%. It is presently unclear why the base does not affect the efficiency in DMSO. Similar observations are apparent with the other substrates.

Overall, DMA when supported by TMEDA is the best solvent. After only 48 h at r.t., the dechlorination of C₆HCl₅ produces predominantly monochlorobenzene (70%) and 1,2-C₆H₄Cl₂ (30%). At longer reaction times, the efficiency will asymptotically approach 80% dechlorination for C₆HCl₅ and 75% for the tetrachlorobenzenes. This corresponds to a 100% yield of monochlorobenzene for both cases³. Compared with our earlier findings in THF [1], a simple change of solvent leads to a more than two-fold increase in activity in terms of dechlorination efficiency.

It is not immediately clear why a mere change of solvent can produce such drastic changes in catalyst activity. It is possible that solvating power plays a major role. DMA, DMF, diglyme (and DMSO to a certain extent) are known to have high dielectric constants and high solvating power. While NaBH₄ is only sparingly soluble in THF, in DMA it dissolves rapidly and exothermically. This leads to better interaction with the reducing agent and facilitates hydride transfer. These solvents have the added advantage in that they are coordinating and help to stabilize the catalytically active species, thus prolonging catalyst lifetime.

While the reaction in DMA without base is very fast at the beginning and then rapidly

subsides, the reaction with the help of TMEDA is initially much slower (not shown) but is more sustainable over a prolonged period. This is attributed to the protective nature of the base towards the active species [Pd⁰(dppf)] [1], giving [Pd⁰(dppf)(tmeda)] which reduces the activity of the catalyst but serves as a reservoir for its gradual release. In the long run, this leads to remarkably higher yields because of the increased lifetime of the catalyst. In fact, it still retains its activity even after 2 weeks of reaction. We tested this by adding fresh C₆HCl₅ and NaBH₄ (the usual amounts) to the reaction mixture. Dechlorination occurred, with the catalytic activity being about half that of a fresh catalyst.

2.2. Selectivity

Table 1 summarizes the selectivity for the dechlorination of the five different polychlorobenzenes using different solvents. Statistically expected product distributions and conversion of substrate and dechlorination efficiency at this reaction time are also included. As discussed in our earlier paper [1], it is apparent that more chlorinated substrates react faster than less chlorinated ones. Selectivity appears to be strongly solvent-dependent. Addition of TMEDA can alter the product distribution in some cases. Under all conditions, C₆HCl₅ does not give rise to 1,2,3,5-C₆H₂Cl₄. Likewise, 1,2,3,5-C₆H₂Cl₄ yields 1,3,5-C₆H₃Cl₃ only in trace quantities. No biphenyl or other coupling product was detected in any of the reactions.

The best-performing DMA, DMF and diglyme exhibit very similar selectivity for C₆HCl₅ and 1,2,3,4-C₆H₂Cl₄ with preferences for 1,2,3,4-C₆H₂Cl₄ and 1,2,3-C₆H₃Cl₃, respectively. In DMF, 1,2,3,5-C₆H₂Cl₄, gives 1,2,3-C₆H₃Cl₃, whereas 1,2,3- and 1,2,4-C₆H₃Cl₃ favor 1,2-C₆H₄Cl₂. Selectivity in these solvents is hence determined by steric factors. The exception is shown in Entry 6 where the formation of 1,4-C₆H₄Cl₂ is higher than expected. Our results for the dechlorination

³ According to the definition of dechlorination efficiency (see footnote 2), a 100% yield of C₆H₅Cl corresponds to $100\% \times 3/4 = 75\%$ dechlorination for C₆H₂Cl₄ and to $100\% \times 4/5 = 80\%$ dechlorination for C₆HCl₅.

of 1,2,4- $C_6H_3Cl_3$ in DMF/TMEDA (Entry 5) are similar to those reported by Zhang et al. [2].

In DMSO or CH_3CN , pentachlorobenzene predominantly yields 1,2,4,5- $C_6H_2Cl_4$. Compared to DMF, the selectivity is remarkably reversed here. For 1,2,3,4- $C_6H_2Cl_4$, a near-equal distribution of products is obtained, except for Entry 21, which shows preference for 1,2,4- $C_6H_3Cl_3$, again different from DMF. In CH_3CN , the selectivity is more or less the same as in DMF for 1,2,3,5- $C_6H_2Cl_4$ and 1,2,3- $C_6H_3Cl_3$. Selectivity for 1,2,4- $C_6H_3Cl_3$ shows a slight preference for 1,2- $C_6H_4Cl_2$.

In THF, the regioselectivity of C_6HCl_5 dechlorination is strongly dependent on base presence. In the absence of a base, 1,2,3,4- $C_6H_2Cl_4$ is the favored product, as in DMF. However, when TMEDA is added, the selectivity is completely reversed, causing a preference for 1,2,4,5- $C_6H_2Cl_4$ like in DMSO. For 1,2,3,4- $C_6H_2Cl_4$, THF shows a strong preference for 1,2,3- $C_6H_3Cl_3$ (similar to diglyme) when no base is used, but in the presence of a base an equal distribution of the possible products is observed. For 1,2,3,5- $C_6H_2Cl_4$, 1,2,3- and 1,2,4- $C_6H_3Cl_3$, THF follows the general trend of the other solvents⁴. These results are significantly different from those of Marques et al. [3].

In our previous paper [1], we introduced the concept of the 'meta-rule', meaning that Cl-atoms with more neighbors in the meta-position are removed preferentially. Comparing the measured product distributions with the statistically expected ratios, we attempted to verify this assumption. Of a total of 42 entries, 24 [Entries 1, 2, 6–12, 14–19, 22–24, 32, 34, 36, 37, 39 and 40] or 57% seem to be consistent with this idea. It is also reasonable to expect a preferen-

tial removal of the sterically least hindered chlorine. Thirty-one entries [3–5, 7–12, 14–18, 20, 22, 25–30, 32, 34 and 36–42] or 74% agree with this steric proposal. In fact, 18 (43%) of the entries agree with both proposals, so that 88% of the results (37 entries) can be explained by either or both. The remaining 12% (five entries) cannot be explained, especially the pronounced selectivity reversal observed for C_6HCl_5 in THF after addition of TMEDA.

While more of our results seem to support a sterically governed selectivity, they do not necessarily contradict the meta-rule as both proposals predict rather similar results. It is clear that the mechanism of this catalytic reaction is very complex and that selectivity is influenced by subtle variations of such parameters as solvent or presence/absence of a base. Simple theories therefore cannot satisfactorily explain the behavior of the system. More work needs to be done in this direction.

A significant outcome of these results (Table 1) suggests that one can control the site selectivity and tailor-design certain products by controlling the reaction conditions. For example, 1,2,3,4- $C_6H_2Cl_4$ is best made by using DMA/TMEDA as the solvent for dechlorination of C_6HCl_5 . After 15 min, the relative concentrations of 1,2,3,4- to 1,2,4,5- $C_6H_2Cl_4$ are 90:10. The absolute yield of 1,2,3,4- $C_6H_2Cl_4$ is 70% at this point. On the contrary, if 1,2,4,5- $C_6H_2Cl_4$ is the desired product, DMSO/TMEDA should be employed. The ratio of 1,2,3,4- to 1,2,4,5- $C_6H_2Cl_4$ is 20:80 after 4 h (yield 50%). Likewise, a 65% yield of 1,2- $C_6H_4Cl_2$ can be obtained after 24 h of dechlorination of 1,2,3- $C_6H_3Cl_3$ in DMF/TMEDA.

3. Conclusion

Our results indicate a remarkable relationship between the efficiency of a catalytic reaction and the solvent used. Pentachlorobenzene, 1,2,3,4- and 1,2,3,5-tetrachlorobenzene, 1,2,3- and 1,2,4-trichlorobenzene were dechlorinated

⁴ Another remarkable feature occurs in THF when the reactants are mixed together in the order substrate, reducing agent, base and finally catalyst. The selectivity is essentially the same as when no base is used. It seems that when the base is added after the reducing agent, it cannot exert its influence on selectivity. Likewise, the yields will drop, as if no base were present.

Table 1
Selectivity and reaction efficiency for dechlorination of various chlorobenzenes

Entry	Substrate	Solvent	Base	Relative concentrations of products ^a								Time (h)	Conversion ^b (%)	Dechlorination ^c (%)	
				12 ^d	13	14	123	124	135	1234	1245				
1 ^e	1,2,4- C ₆ H ₃ Cl ₃	THF	TMEDA	40	20	40						90 ^f	100	37	
2			none	40	20	40						26	12	4	
3		CH ₃ CN	TMEDA	50	20	30						94	70	21	
4			none	60	20	20						77	18	5	
5		DMF	TMEDA	70	15	15						24	89	35	
6			none	40	15	45						28	21	7	
exp ^g		–	–	33	33	33									
7 ^e	1,2,3- C ₆ H ₃ Cl ₃	THF	TMEDA	90	10							160	27	9	
8			none	95	5							46	14	5	
9		CH ₃ CN	TMEDA	90	10							94	77	21	
10			none	95	5							77	16	6	
11		DMF	TMEDA	95	5							23	72	27	
12			none	95	5							28	32	12	
exp		–	–	67	33										
13	1,2,3,5- C ₆ H ₂ Cl ₄	THF	TMEDA				20	80	–			43	98	30	
14			none				30	70	trace			93	95	26	
15		CH ₃ CN	TMEDA				40	60	–			47	81	24	
16			none				35	60	5			71	45	12	
17		DMF	TMEDA				40	60	–			23	92	26	
18			none				40	60	trace			50	94	28	
exp		–	–				25	50	25						
19 ^e	1,2,3,4- C ₆ H ₂ Cl ₄	THF	TMEDA				50	50				70	58	16	
20			none				80	20				46	30	8	
21		CH ₃ CN	TMEDA				35	65				94	88	24	
22			none				60	40				90	58	15	
23		DMSO	TMEDA				40	60				90	89	25	
24			none				50	50				120	86	26	
25		diglyme	TMEDA				70	30				24	89	28	
26			none				80	20				49	58	16	
27		DMF	TMEDA				80	20				0.5	93	38	
28			none				75	25				23	61	22	
29	DMA	TMEDA				80	20				20	66	20		
30		none				90	10				24	85	27		
exp		–	–				50	50							
31 ^e	C ₆ HCl ₅	THF	TMEDA							30	70 ^h	20	100	26	
32			none							80	20	46	29	6	
33		CH ₃ CN	TMEDA							35	65	3	86	20	
34			none							40	60	70	89	23	
35		DMSO	TMEDA							20	80	4	100	29	
36			none							45–60 ⁱ	40–55	4	100	29	
37		diglyme	TMEDA							70	30	22	100	33	
38			none							90	10	19	100	23	
39		DMF	TMEDA							80	20	0.8	100	22	
40			none							80	20	0.7	100	25	
41		DMA	TMEDA							90	10	0.3	100	25	
42			none							90	10	0.5	100	35	
exp ^j			–	–						40	20				

in THF, acetonitrile, DMSO, diglyme, DMF and DMA with or without the presence of TMEDA. It was in DMA/TMEDA, however, that we found a more than two-fold enhancement over our previous result [1], where THF/TMEDA was used. In DMA/TMEDA, C_6HCl_5 was dehalogenated to predominantly monochlorobenzene within 48 h by mere stirring at room temperature. The solvents studied can be ranked in order of decreasing performance as follows: DMA > DMF > diglyme > DMSO > CH_3CN > THF. High solvating potency (with respect to catalyst and reducing agent) and strong coordinating capability (to stabilize the catalyst) are conceivably significant factors that lead to the excellent performance of DMA and DMF. In all cases, except DMSO, addition of TMEDA enhances the dechlorination reaction. In DMA/TMEDA, the catalyst retains its activity even after 2 weeks of reaction. This indicates a dual-pronged stabilizing effect on the catalyst via solvent and base.

Not only catalytic efficiency, but selectivity as well is influenced by a change in solvent. In this manner, selectivity can be tuned by a judicious choice of conditions. In DMA/TMEDA for example, if the reaction is stopped after 15 min, 1,2,3,4-tetrachlorobenzene will be formed in 70% yield. If the other product is desired, one can employ DMSO/TMEDA and obtain 50% 1,2,4,5-tetrachlorobenzene after 4 h. Selectivity is also influenced by the base. This is most evident when C_6HCl_5 is dechlorinated in THF. Addition of TMEDA leads to a complete rever-

sal in selectivity. To find an explanation for this stunning phenomenon shall be the object of our further investigations.

4. Experimental

All reactions were carried out under nitrogen and standard Schlenk techniques were used. Dppf [7,8] and $PdCl_2(dppf)$ [9,10] were synthesized according to literature methods. Chlorinated benzenes were obtained from Aldrich, except for 1,2,3,5-tetrachlorobenzene, which was bought from Supelco. Solvents were purchased from J.T. Baker (THF, DMSO, CH_3CN), Fluka (diglyme), Merck (DMA) and BDH (DMF) and used without prior distillation. In a typical reaction, the substrate (1 mmol) was dissolved in freshly degassed solvent (20 ml) together with $PdCl_2(dppf) \cdot CH_2Cl_2$ (0.037 g, 0.045 mmol). Upon addition of TMEDA (2 ml, 13.4 mmol, excess), $NaBH_4$ (0.19 g (5 mmol) per mmol 'Cl') was added (0.57, 0.76 and 0.95 g for tri-, tetra- and pentachlorobenzene, respectively). The suspension was stirred for several days at r.t. and samples of ca. 0.5 ml were withdrawn periodically by filtering through a Teflon delivery tube. The sample was diluted to 10 ml with THF and analyzed with a Hewlett Packard 5890 series II gas chromatograph (column HP1, cross-linked methyl silicone gum, 25 m \times 0.32 mm \times 0.52 μ m film thickness). Temperature program: 32°C, hold for 5 min, heat at 10°C/min to 260°C, hold for 1 min. The injec-

Notes to Table 1:

^aRelative concentrations of first dechlorination products in percent taken at highest yield of main product; averages of several runs.

^bConversion of substrate (100%-current substrate concentration).

^cDechlorination efficiency, see footnote 2 in main text.

^d12 = 1,2-dichlorobenzene, etc.

^eFrom Ref. [1].

^fReflux conditions (67°C).

^gExpected ratio from statistical probability.

^hNo 1,2,3,5-tetrachlorobenzene was formed.

ⁱPoor reproducibility.

^jThe expected value for 1,2,3,5-tetrachlorobenzene would be 40%.

tor was held at 200°C, the FID detector at 250°C. A Shimadzu QP5000 GC/MS was used to confirm peak identity.

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