

The KGME Process¹ - A New Method for The Chemical Destruction of Haloaromatics

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ABSTRACT:

The reaction of 2-methoxyethanol with either KOH or KH in an aprotic solvent results in the formation of the potassium derivative, KGME. This reagent reacts with haloaromatics, replacing one or more halogens with the 2-methoxyethoxy functionality. Chlorobenzenes, PCBs, PCDDs and PCDFs have been destroyed using KGME. A comparison of this reagent with the standard nucleophile, KPEG, is presented.

INTRODUCTION:

Over the past decade, a number of processes²⁻⁵ have been developed which employ a strong nucleophile to displace one or more halogens from toxic environmental pollutants such as PCBs, PCDDs and PCDFs. Most of these utilize an alkali metal (usually potassium) derivative of one of a number of polyethylene glycols (usually PEG 400). While the nucleophile KPEG is effective in reducing the levels of many aromatics, dioxins and furans, in practice it is usually employed in large molar excesses, producing an enlargement in the size of the waste stream for ultimate land disposal, or incineration. The increased cost of additional nucleophile, coupled with concomitantly high disposal costs, led us to explore the use of alternate, potentially more cost-effective reagents.

EXPERIMENTAL SECTION:

Analytical - Gas chromatographic data for analysis of reaction mixtures were obtained by gas chromatography using a DB5 capillary column, with FID for chlorobenzenes (biphenyl as internal standard), or ECD for PCBs (EPA method 8080). PCB concentrations are corrected for reagent and solvent dilutions.

s-Trichlorobenzene Dehalogenation - To a 250 mL three neck round bottom flask equipped with mechanical stirrer, reflux condenser and thermometer, were added 30 mL toluene and 0.05 mole each of the appropriate alkali metal hydroxide and alkoxyalcohol (Table 1). The dehalogenation reagent was performed by heating this mixture to reflux with stirring for 15 minutes. (If toluene distilled over CaH_2 was used, then KH could be substituted for KOH to form the potassium derivative). After cooling the reaction mixture to ambient temperature, the appropriate amount of 1,3,5-trichlorobenzene (Table 1) and the internal standard were added to the flask, and the reaction mixture was heated to reflux. About 1 mL aliquots were withdrawn at the desired time period and were diluted with 3 mL toluene and washed thrice with 50 mL water. The toluene phase was then dried over MgSO_4 , filtered and analyzed (Table 1).

DMSO - Assisted KGME Dehalogenation Reactions of Chlorobenzenes - To a 250 mL flask equipped as in the above example were added 2.25 g (0.02 mole) chlorobenzene, 6.75 g (0.046 mole) m-dichlorobenzene and 11.25 g (0.062 mole) 1,3,5-trichlorobenzene. A mixture of 22.83 g (0.3 mole) 2-methoxyethanol and 18.70 g (0.3 mole) potassium hydroxide were added with stirring, followed by the molar quantity of dimethyl sulfoxide, and in some cases 80.0 g of a solvent, as shown in Table 2. The reaction mixture was heated in an oil bath to the specified temperature. After three hours of stirring and heating, a 1.00 g aliquot was removed and diluted with 1.00 mL of a toluene solution containing 4.000 g biphenyl/100 mL toluene. An additional 2 mL toluene were added and the sample was washed, dried and analyzed.

PCB Destruction Reactions - PCB-containing oils (aroclor) were analyzed for % Cl. A quantity of sample was weighed into an appropriate size three neck flask (equipped as in the first example). A quantity of 2-methoxyethanol and potassium hydroxide equivalent to the number of gram-atoms of chlorine was added to the flask, which was then heated with stirring, in an oil bath for the time and temperatures shown in Table 3.

RESULTS AND DISCUSSION.

Table 1 illustrates the effect of alkali metal derivatives of various alkoxyalkanols on the dehalogenation of s-trichlorobenzene (TCB). Clearly, the potassium derivative (KGME) is more effective than the corresponding sodium derivative (NaGME) for the dehalogenation of TCB. Furthermore, reactivity decreases with increasing size of the R group in $\text{ROCH}_2\text{CH}_2\text{OK}$. The reagent shown in entry 6 is the potassium derivative of a secondary alcohol, and is less reactive than the other primary alcohol derivatives for steric reasons. When a TCB/KGME reaction is allowed to proceed to completion, one obtains about a 98% yield of 1,3-dichloro-5-(2-methoxyethoxy)benzene, and about a 1% yield of the disubstituted product, 1,3-bis(2-methoxyethoxy)-5-chlorobenzene. Both products were identified by gc/ms.

TABLE 1 - Alkoxyalkanol/Alkali Treatment of s-Trichlorobenzene at 111°C

No.	Dechlor Reagent	Reagent:TCB - molar ratio	% Dechlor TCB	Time (hours)
1	$\text{MeOCH}_2\text{CH}_2\text{OK}$ (KGME)	3:1	98.4	0.5
2	$\text{MeOCH}_2\text{CH}_2\text{OK}$ (KGME)	3:2	72.4	0.5
3	$\text{MeOCH}_2\text{CH}_2\text{ONa}$ (NaGME)	3:1	80.4	4.0
4	$\text{EtOCH}_2\text{CH}_2\text{OK}$	2:1	79.2	2.0
5	$n\text{-BuOCH}_2\text{CH}_2\text{OK}$	2:1	53.2	2.0
6	$\text{MeOCH}_2\text{CH}(\text{Me})\text{OK}$	2:1	55.0	6.0

Table 2 demonstrates the accelerative effect of dimethyl sulfoxide addition, as well as the effect of various solvents, on the dechlorination of a mixture of mono-, di- and trichlorobenzenes. This effect has been long known for nucleophilic substitution reactions⁶, and has been recently demonstrated for KPEG dehalogenation in particular⁵.

TABLE 2 - Effect of DMSO/Solvent on Chlorobenzenes/KGME Reaction

No.	Solvent (80 g)	DMSO (moles)	Temp. (°C)	Time (hrs)	% Destruction		
					CB	m-DCB	a-TCB
1	none	0.05	115	3.0	<1	19.1	100
2	none	0.30	"	"	"	42.4	100
3	none	0.60	"	"	"	57.9	100
4	none	1.20	"	"	"	71.0	100
5	xylene	0.30	"	"	"	43.7	100
6	"	0.15	"	"	"	4.4	100
7	kerosene	0.15	"	"	"	31.0	90.0
8	mineral oil	0.15	"	"	"	20.0	100
9	mineral oil	1.00	"	"	7.8	80.9	100
10	mineral oil	0.50	130	6.0	10.7	83.9	100
11	mineral oil	1.00	"	"	14.3	94.7	100
12	glyme	0.15	"	"	<1	8.6	77.4
13	n-BuOH	0.15	"	"	<1	6.3	31.2

Increasing the concentration of DMSO causes an increase in the conversion of DCB to 1-chloro-3-(2-methoxyethoxy)benzene (entries 1-4). The former compound is virtually non-reactive in the absence of DMSO. The observed effect that polar protic solvents such as n-butanol and glyme appear to be less effective than apolar solvents in promoting DMSO catalyzed KGME dechlorination can be explained by the fact that protic reagents can solvate the 2-methoxyethanolate anion, thereby reducing its nucleophilicity. The sulfoxide exerts its greatest effect in the least polar solvents. Only in mineral oil, at rather high DMSO concentrations, was there any dehalogenation of monochlorobenzenes.

Table 3 shows the effect of KGME treatment on some PCB-containing, as well as dioxin/furan containing wastes. A KPEG treatment is shown for comparison. Both KGME and KPEG are capable of reducing highly chlorinated PCB congeners, such as those found in aroclors 1260 and 1254, from initial concentrations of >100,000 ppm to post treatment levels of <10 and frequently <1 ppm. Neither reagent will react so effectively with lower congeners such as those found in aroclors 1016 and 1242, and treatment of these materials usually requires large reagent excesses and greatly increased reaction times and temperatures.

The dehalogenation shown as entry 4 in Table 3 was performed on a waste which contained 722 ppb of PCDDs and 2725 ppb of PCDFs prior to treatment. After 1.25 hours at 115°C (one equivalent KGME/equivalent Cl; 0.5 equivalent of 2-methoxyethanol excess), the dioxins and furans were reduced to below limits of detection (<1 ppb). A similar treatment with KPEG resulted in a comparable destruction of dioxins, however the levels of tetrachlorinated dibenzofurans were actually increased (from 30 to 251 ppb).

TABLE 3 - Destruction of PCBs

No.	Reagent	Initial PCBs (ppm)	Final PCBs (ppm)	Temp. (°C)	State
1	KGME*	256,000 ^a	10,200 ^b	115	oil
2	KGME*	256,000 ^a	9,800 ^b	145	oil
3	KPEG*	256,000 ^a	17,900 ^b	115	oil
4	KGME	600,000	35,400	115	oil
5	KGME**	35,800 ^c	3,900 ^d	150	solid

* [5 hours, ratio of reagent:oil = 5.56 (w:w)]

** [5 hours, ratio of solvent (diesel oil):reagent:solid = 4:2:1 (w:w:w)]

a aroclors 1260: 152,600 ppm; 1254: 47,100 ppm and 1242: 56,900 ppm

b aroclor 1242, only; aroclors 1254 and 1260 <5 ppm each

c aroclors 1254: 9,800 ppm; 1016: 26,000 ppm

d aroclor 1016, only

At equal weights of reagent (entries 1 and 3, Table 3) KGME is more effective than KPEG in destroying PCBs. At equimolar concentrations, KPEG treatment is more effective, but considerably more expensive as well. On an equimolar basis, nearly four times the weight of KPEG is required to dehalogenate a given PCB sample, with respect to KGME. As a further consequence of the considerable differences in molecular weight, KPEG also generates a much larger waste stream for ultimate disposal than does KGME. Finally the KGME treated reaction mixture and waste stream are much more fluid and easier to handle than is the KPEG treated one, making KGME treatment a more facile and cost effective method of PCB destruction than KPEG.

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