PERGAMON

Chemosphere 41 (2000) 907–916

CHEMOSPHERE

Destruction of halogenated hydrocarbons with solvated electrons in the presence of water

Guang-Ri Sun, Jin-Bao He, Charles U. Pittman Jr. *

Department of Chemistry, University/Industry Chemical Research Center, Mississippi State University, Mississippi State, MS 39762-9573, USA

Received 25 June 1999; accepted 1 September 1999

Abstract

Model halogenated aromatic and aliphatic hydrocarbons and halogenated phenols were dehalogenated in seconds by solvated electrons generated from sodium in both anhydrous liquid ammonia and ammonia/water solutions. The minimum sodium required to completely dehalogenate these model compounds was determined by increasing the Na/substrate ratio until halogen loss was complete. Minimum sodium consumptions were determined in both anhydrous liquid ammonia and with a (5, 20, 50-fold molar excess of water per mole of halide). While more Na was consumed in the presence of water, these dehalogenations were still efficient when a 50-fold water excess was present. Dehalogenation is faster than competiting reactions with water. CCl_4 and CH_3CCl_3 in the presence of a stoichiometric deficiency of sodium produced only CH_4 and CH_3CH_3 and recovered CCl_4 or CH_3CCl_3, respectively. No partially dechlorinated products were detected, indicating dechlorination was diffusion controlled. Na consumption per chlorine removed (as NaCl) was lower than that of Li, K or Ca and this advantage increased in the presence of water. Na consumption was lower using Na chunks instead of a thin Na mirror. Chloroaromatic compounds gave the parent aromatic hydrocarbon and aminated products in anhydrous ammonia but aminated products did not form when water was present.

Keywords: Solvated electron reductions; Dechlorination; Dehalogenation; Na/NH_3; Chlorinated-aliphatic and aromatic hydrocarbons

1. Introduction

Halogenated organic compounds, such as solvents, pesticides, herbicides, PCBs, CFCs, etc. have caused serious environmental problems. PCBs, for example, are distributed in soils, sludges, estuaries, etc. at over 400 sites and chlorinated aliphatic hydrocarbons (CAHs) are serious contaminants at 358 major hazardous waste sites in the United States. PCBs are regulated under TSCA (Toxic Substances Control Act, 1976). Chemical destruction has been carried out by incineration, wet air oxidation and catalytic dehydrochlorination reaction with superoxide, photolysis and electrolytic reduction. Metal-promoted borohydride or alkoxyborohydride reductive dechlorination (Tabaei and Pittman, 1993a,b; Tabaei et al., 1992), Ti-catalyzed borohydride dechlorination (Liu et al., 1995), iron-promoted dechlorination (Chung et al., 1995), borohydride reductive dechlorination in glymes (Yang and Pittman, 1997, 1998a,b) and thermolysis over solid bases like $CaO/Ca(OH)_2$ (Yang and Pittman, 1996) were recently developed. However, serious limitations exist and many methods cannot be used economically with soils.

Alkali metal-based reductive dehalogenation is a well known process. Knorre et al. (1980) added sodium to the halogenated organic compounds without solvent, but

---

* Corresponding author. Tel.: +1-601-325-7616; fax: +1-601-325-7611.

E-mail address: cpittman@ra.msstate.edu (C.U. Pittman Jr.).

0045-6535/00/$ - see front matter
PII: S0045-6535(99)00428-2

this heterogeneous reaction is slow and moisture sensitive. Dissolving Li, Na, K or Ca in liquid NH_3 generates solvated electrons which dehalogenate dissolved organic compounds at exceptionally fast rates (Watt, 1950; Birch and Subba Rao, 1972; Aiired et al., 1974; Lahaniatis et al., 1975; Jessup et al., 1977).

Both Commodore Solution Technologies (Weinberg and Abel, 1989, 1992) and our group (Pittman and Tabaei, 1993, 1994; Pittman and Mohammed, 1996) have demonstrated that neat PCBs and PCB-contaminated soils (as received clay, loam and sandy soils containing up to 30% water) can be decontaminated in liquid ammonia slurries by adding Na or Ca. PCB-destruction efficiencies >99.9% were achieved within 30 s at room temperature (Weinberg and Abel, 1989, 1992; Pittman and Tabaei, 1993, 1994; Pittman and Mohammed, 1996). These results indicate that Na/NH_3 or Ca/NH_3 dechlorinations are significantly faster than reactions with water. Soils typically contain water, oxygen and iron, all of which can interfere with solvated electron chemistry (Eastham and Larkin, 1959; Smith, 1968; Rabideau et al., 1984). Both oxygen and iron catalyze the reaction of Na and Ca with ammonia to produce the metal amide salt and hydrogen. The half-life ($t_{1/2}$) of solvated electrons in purified NH_3 is ca. 300 h (Crooks and Bard, 1987), but in pure water the solvated electron has a $t_{1/2}$ of ca. 100 µs. (Gould, 1965). Dechlorination of PCB-contaminated wet soils is possible due to the relatively long solvated electron lifetime in 20% H_2O/80% NH_3 ($t_{1/2}$ = ca. 100s (Schindewolf, 1970; Crooks and Bard, 1987)) coupled with fast dechlorination by $Na/NH_{3(L)}$ (Weinberg and Abel, 1989, 1992; Pittman and Tabaei, 1993, 1994; Pittman and Mohammed, 1996).

No systematic study has appeared of solvated electron dechlorinations in $NH_{3(L)}$ with excess water present. PCBs, CAHs, etc. intercalated deep in clay layers require diffusion of solvated electrons into soil or extraction of chlorinated organics into the bulk solution. This could allow time for competitive reactions with water. Competitive reactions may accelerate in the presence of oxygen, transition metal ions, acidic soil sites, etc. Therefore, we determined the consumption of Na required to acheive complete dechlorination of both chloroaromatic and chloroaliphatic compounds in the presence of excess water. The reactivity of Li, Na, K and Ca was also briefly compared.

2. Experimental

2.1. Material and equipment

Ammonia was purchased from Dupont, National Ammonia Division. It was condensed from a steel tank into a stainless cylinder (1 l) containing calcium metal. After drying over Ca, ammonia was distilled and condensed into a smaller stainless cylinder (120 ml). 4-Chlorophenol, 4-fluorophenol, 4-bromophenol, 2-chloro-4-fluorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, chlorobenzene, 1,2-dichlorobenzene, 1,2,3-trichlorobenzene, 1,2,3,4-terachlorobenzene, 4-chlorotoluene, 3,4-dichlorotoluene, 2-chloro-*p*-xylene, 2bromo-*p*-xylene, 3-fluoro-*o*-xylene, 1-chlorooctane, 1,1,1-trichloroethane, carbontetrachloride and 1,2,3,4,5,6-hexachlorocyclohexane, octane, decane, dodecane, diethylether, *p*-xylene, sodium, lithium, potassium and calcium were purchased (Aldrich) and used as received.

Reactions were run in glass pressure vessels (Andrews Glass) All valves and conduits were stainless steel (90 ml, maximum safe pressure 200 psi).

2.2. Dehalgenation reactions

All dehalogenation reactions were carried out by Procedure A, unless otherwise stated. Procedures B, C, D and E were used for comparison with Procedure A. Two work-up protocols, Method 1 and Method 2, were used as described below. All data in Tables 1–8 were determined from at least two (and many cases more) experiments.

Procedure A: Halocarbon (1 mmol) and metal (particle size, >8 mm^3) were added, under nitrogen, to vessel A equipped with a glass covered stirring bar. Ammonia (10 ml) and water (or just ammonia) were added to vessel B. The pressure in vessel B was raised to 160 psi with nitrogen from a cylinder. Vessel B (upside down) was connected from above to vessel A via a metal conduit (Fig. 1). Ammonia was discharged, all at once, from B into A by the higher pressure in B. The contents of A were vigorously stirred before and after addition for 30 s at room temperature. Sodium dissolution was complete before 30 s.

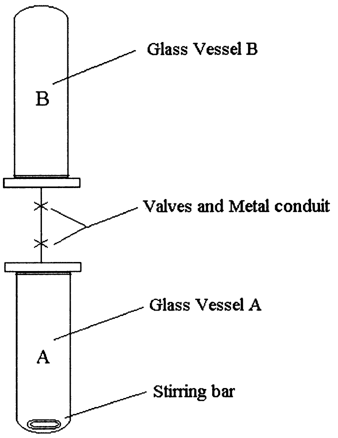


Fig. 1.

Procedure B: Procedure B was similar to Procedure A except that both substrate (1 mmol) and ammonia were added into vessel B. The vessel B was shaken vigorously to dissolve the substrate in $NH_{3(L)}$ or NH_3/H_2O solution. Then, this solution was added all at once to vessel A containing sodium with vigorous stirring.

Procedure C: Metal was added, under nitrogen, into vessel A, equipped with a glass stir bar. Liquid ammonia (10 ml) was then added and stirred at ambient temperature until the metal was completely dissolved. Ammonia was slowly evaporated at room temperature to generate a thin silver sodium mirror in vessel A. Substrate (1 mmol) was added to the sodium mirror. Then $NH_{3(L)}$ or NH_3/H_2O was rapidly added to A from B while vigorously stirring. Stirring was continued for 30 s at room temperature.

Procedure D: Na/NH_3 was generated in vessel B from a specific weight of sodium and liquid ammonia (10 ml). This solution was added with vigorous stirring, at ambient temperature, to a preformed substrate (1 mmol)/ NH_3 (5 ml) or NH_3/H_2O (5 ml) solution in vessel A at different H_2O/substrate ratios and stirred at room temperature for 30 s.

Procedure E: Substrate (1 mmol), water and liquid ammonia (10 ml) were added to vessel A at room temperature. After cooling to −55°C, sodium was added all at once while stirring. Stirring continued at −55°C for 30 s.

Work-up: Method 1 was used with halogenated xylenes and phenols. Method 2 was used with aliphatic chlorides, chlorobenzenes and chlorotoluenes.

Method 1: After dehalogenation, ammonia was slowly evaporated at room temperature. The resulting residue was extracted with ether (10 ml). In chlorophenol reactions, the residue was neutralized with H_2SO_4 (15% (w/w) aq.) prior to extraction with ether.

Method 2: After dehalogenation, water (30 ml) was added to dilute the $NH_{3(L)}$. Then the mixture was extracted with ether (15 ml) at −20°C to 0°C. In the dehalogenations of CCl_4 and CH_3CCl_3, *p*-xylene (10 ml) was used for extraction. The organic phase was separated after shaking vigorously for several minutes. In dechlorinations of CCl_4 or CH_3CCl_3, a gas sample was taken with a pressure syringe to identify CH_4 or CH_3CH_3 before separation.

2.3. Analysis

Capillary GC (Varian model 3300) determined conversions and identified and quantified products using both Supel-Q PLOT fused silica (30 m, 0.32 mm ID) and DB-5 (30 m, 0.32 mm ID) columns with *n*-octane, dodecane and hexadecane internal standards. Minimum conversion data were >99%, unless otherwise stated. GC–MS analysis was performed on a Finnigan 4500 GC–MS. Chloride analysis was carried out after reductions as described below.

Chloride analysis procedure: After dehalogenation and work-up by Method 2, H_2O/NH_3 was removed in vacuo. Sodium chloride residue remained. Distilled water was added to this residue to give 150 ml of solution. Then, concentrated nitric acid (1 ml) was added. This solution was titrated at room temperature with $AgNO_3$ (0.1 N) until no further silver chloride precipitate formed. The solution was heated to reflux for 5–10 min, cooled and allowed to stand for 2 h. AgCl precipitate was collected, rinsed with HNO_3 aq. (1.2% (w/w), 10 ml) and distilled water (10 ml × 2), dried in vacuo at 70°C for 8–15 h and weighed.

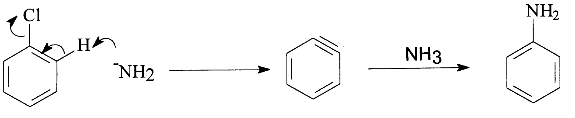
3. Results and discussion

3.1. Product distributions

Eighteen aliphatic and aromatic halogenated model compounds were completely dehalogenated in seconds by solvated electrons. These reductions required only the time needed to dissolve the metal. Room temperature reductions of six chlorinated aromatic molecules in anhydrous $NH_{3(L)}$ are summarized in Table 1. Products consist of the parent hydrocarbon and an amminated product in each case except for 4-chlorophenol which produced phenol.

General mechanistic features for these dehalogenations are summarized in Scheme 1. Rapid electron transfer to aromatic halides generates an anion radical. Then, loss of halide ion gave an aromatic radical. This radical might abstract hydrogen, dimerize or acquire another electron to form an aryl anion which then abstracts a proton to give ArH. Dimerization products were not detected. This scheme accounts for the hydrocarbon products (Table 1). The aminated products, formed when the solvent was anhydrous $NH_{3(L)}$, could result from a benzyne route (Eq. (1) where the base could be either NH_2^- or Ar^-) or from NH_2^- addition to the intermediate aryl radical (as shown in Eq. (2) for chlorobenzene) followed by rapid electron transfer. Aminated product yields increased when both substrate and sodium concentrations were increased, a result consistent with either pathway. This is illustrated in Table 1 upon comparing entries 1 with 1a and 3 with 3a.

Reduction of 4-chlorotoluene (Eq. (3)) gave mostly toluene but approximately equal amounts of *m*- and *p*-toluidine were formed, consistent with a benzyne intermediate. No animated products were produced when water was added. Water protonates $^-NH_2$ removing the benzyne route.



(1)

Table 1
Products from Na/NH_3 dechlorinations of model chlorinated aromatic substrates at 25°C[a]

Entry	Starting materials	Hydrocarbon products (mol%)	Aminated products (mol%)	Other unknown products[b]
1	Chlorobenzene[c]	Benzene (88%)	Aniline (10%)	(2%)
1a	Chlorobenzene[b]	Benzene (84%)	Aniline (15%)	(1%)
2	1, 2-Dichlorobenzene[c]	Benzene (73%)	Aniline (25%)	(2%)
3	4-Chlorotoluene[c]	Toluene (87%)	*m*-Toluidine (5%) *p*-Toluidine (5%)	(3%)
3a	4-Chlorotoluene[c]	Toluene (85%)	*m*-Toluidine (7%) *p*-Toluidine (7%)	(1%)
4	3, 4-Dichlorotoluene[c]	Toluene (47%)	*m*-Toluidine (18%) *p*-Toluidine (32%)	(3%)
5	3, 4-Dichlorotoluene[c]	Toluene (100%)[d]		
6	2-Chloroxylene[e]	*p*-Xylene(60%)	2-Aminoxylene (37%)	(3%)
7	4-Chlorophenol[e]	Phenol (98%)		(2%)

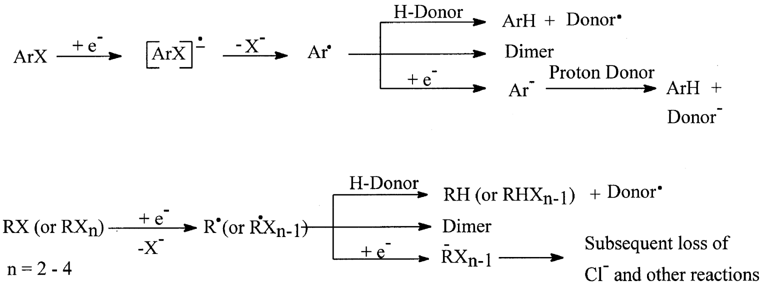
[a] Conducted by Procedure A where substrate (1 mmol), $NH_{3(L)}$ (10 ml) and Na (1.5–2.8 mmol) were employed. However, entries 1a and 3a employed substrate (2 mmol), $NH_{3(L)}$ and Na (4 mmol). Reproducibility in these experiments was ±3%.

[b] Traces of several kinds of unknown products.

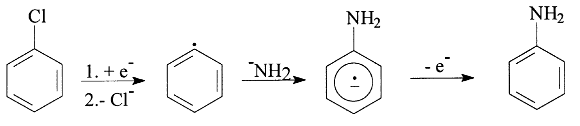
[c] Work-up by Method 2.

[d] Reduction was carried out in the presence of water where substrate (1 mmol), $NH_{3(L)}$ (10 ml), H_2O (5 mmol) and Na (4.2 mmol) were employed.

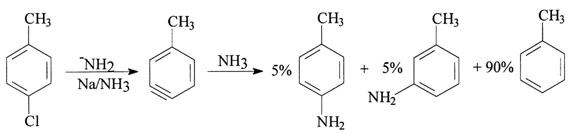
[e] Work-up by Method 1.



Scheme 1.

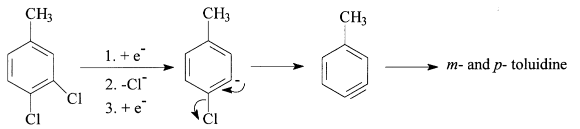


(2)



(3)

The yield of aminated products increased as the number of ring chlorines increased. 3, 4-Dichlorotoluene produced a mixture of *m*-toluidine (18%) and *p*-toluidine (32%) (50% of the total yield) when treated with Na/NH_3 at a substrate concentration of 1 mmol in 10 ml NH_3. For comparison, 4-chlorotoluene only gave 10% of *p*- and *m*-toluidines at these conditions. The intermediate anion formed after loss of the first chlorine might eliminate a second Cl^- to produce a benzyne (Eq. (4)).



(4)

In contrast, dehalogenation of chlorophenol gave no aminated products. Furthermore, aryl chloride dechlorinations with Na/NH_3 in the presence of added water gave no aminated products because NH_2^- was protonated by water or phenol, removing amide and preventing amination via Eqs. (1) or (2).

3.2. Minimum Na consumption required for complete dechlorination

The minimum amount of sodium required to completely dechlorinate both aromatic and aliphatic compounds was determined by the stepwise increase of the Na/substrate ratio in several reactions until complete chlorine loss occurred. This ratio was obtained both in anhydrous liquid ammonia and in the presence of water (5, 20, 50-fold molar excess of water per mole of halide). Representative results are summarized in Table 2 for monochloroaryl compounds (entries 1–3), di-, tri- and tetrachloroaryl compounds (entries 4–7), chlorinated phenols (entries 8–10) and chlorinated aliphatic compounds (entries 11–14).

All dechlorinations required more than one equivalent of Na to complete in anhydrous $NH_{3(L)}$. This might be due to:

1. reaction of solvated electrons, with NH_3 to generate NH_2^-, catalyzed by traces of Fe^{3+},
2. formation of aryl carbanions (after loss of chlorine) or
3. competiting reactions with water (last 3 columns, Table 2).

Aryl carbanion formation consumes two electrons per chloride lost. The most important finding is that adding substantial amounts of water did not greatly increase the amount of Na needed for complete dehalogenation. Dehalogenation was faster than reaction of solvated electrons with water (Watt, 1950; Birch and Subba Rao, 1972; Aiired et al., 1974; Lahaniatis et al., 1975; Jessup et al., 1977). The data in Table 2 demonstrate this point. A total of 1.5 equivalents of sodium are required to completely reduce chlorobenzene to benzene. However, adding a 50 mol excess of water only increased the sodium requirement to 2.5 equivalents (entry 1). In CCl_4 dechlorinations only 4.6 equivalents of Na per CCl_4 (1.15 equivalents Na per Cl) were needed to reduce CCl_4 to CH_4 when no water was added. Adding a 50 mol excess of water versus CCl_4 increased the sodium requirement to only 6.4 equivalents (1.6 equivalents Na per Cl, entry 14). Similar results were obtained for the other chlorides (entries 2–7, 12–14) except for chlorooctane (entry 11) and the chlorophenols (entries 8–10).

The chlorophenols apparently consumed one extra mole of Na to generate the corresponding phenoxide anions (or react with NH_4^+). Chlorinated phenoxide anions should be difficult to reduce due to the delocalized negative charge. The data in entries 8–10 (Table 2) show a higher sodium consumption per chlorine removed, supporting this point. For example, when no water was added, 4-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol required 2, 1.7 and 1.53 equivalents of Na, respectively, per chlorine removed. However, chlorobenzene, 1.2-dichlorobenzene and 1,2,3-trichlorobenzene only required 1.5, 1.4 and 1.33 equivalents of Na, respectively, per chlorine removed. Increasing chlorine substitution leads to a decreased consumption of Na per chlorine lost, both with and without water present.

The Na required for total dehalogenation of 1-chlorooctane increased from 1.7 to 4 equivalents upon

Table 2
Minimum amount of Na required to completely dechlorinate chloroaromatics at 25°C[a]

Entry substrate	Na/substrate mole ratios and (Na/Cl removed) required for complete dechlorination at different H_2O/substrate mole ratios				
	H_2O/substrate →	0/1[b]	5/1	20/1	50/1
1	Chlorobenzene	1.5 (1.5)[c]	2.3	2.4	2.5 (2.5)[c]
2	4-Chloro-toluene	1.5 (1.5)[c]	2.3	2.4	2.5 (2.5)[c]
3	2-Chloro-*p*-xylene	1.5 (1.5)[c]	2.3	2.4	2.5 (2.5)[c]
4	1,2-Dichlorobenzene	2.8 (1.4)[c]	4.0	4.5	5.0 (2.5)[c]
5	3,4-Dichlorotoluene	2.5 (1.25)[c]	4.2	4.6	6.0 (3)[c]
6	1,2,3-Trichlorobenzene	4.0 (1.33)[c]	5.5	5.8	7.0 (2.33)[c]
7	1,2,3,4-Tetrachlorobenzene	5.0 (1.25)[c]	6.5	7.0	8.6 (2.15)[c]
8	4-Chlorophenol	2.0 (2)[c]	2.9	4.0	4.5 (4.5)[c]
9	2,4-Dichlorophenol	3.4 (1.7)[c]	5.0	5.6	8.0 (4)[c]
10	2,4,6-Trichlorophenol	4.6 (1.53)[c]	7.4	8.0	10 (3.33)[c]
11	1-Chlorooctane	1.7 (1.7)[c]	2.3	2.5[d]	4.0[d] (4)[c]
12	1,1,1-Trichloroethane	3.6 (1.2)[c]	4.2	4.5	5.1 (1.7)[c]
13	Carbontetrachloride	4.6 (1.15)[c]	5.1	5.5	6.4 (1.6)[c]
14	Lindane	6.7 (1.11)[c]	6.7	7.2	7.4 (1.23)[c]

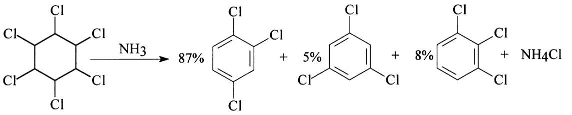
[a] Experiments were conducted by Procedure A unless, otherwise, stated.

[b] No water added.

[c] Moles of Na consumed per mole of chlorine removed, derived from Na/substrate weighings and divided by the number of chlorines in the substrate. Estimated errors ±4%.

[d] Experiments were performed using Procedure B.

adding a 50 mol excess of water (entry 5). In contrast, the Na consumption per chlorine for complete dehalogenation of lindane (1, 2, 3, 4, 5, 6-hexachlorocyclohexane) increased from 1.11 with no water to 1.23 equivalents with a 50 mol excess of water (entry 15). Lindane might undergo E-2 eliminations of up to 3 mol of HCl in the presence of NH_3 and/or NH_2^-. Dissolving lindane (1 mmol) in ammonia (10 ml) at ambient temperature for 5 min with no Na present gave a 99% total conversion to 1, 2, 4-trichlorobenzene (87%), 1, 3, 5-trichlorobenzene (5%) and 1, 2, 3-trichlorobenzene (8%) (Eq. (5)).



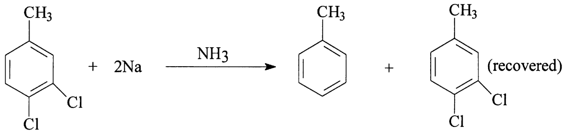
(5)

E-2 elimination may compete with dissociative electron transfer during the reduction of lindane in Na/NH_3. Fast dissociative electron transfer would produce radicals which, upon abstraction of hydrogen, would result in chloroaliphatic intermediates. They might undergo subsequent E-2 elimination with NH_3, after Na had been consumed, leading to lower Na consumption. Transfer of the electron to RCl with simultaneous loss of chloride occurs for chlorinated aliphatic compounds (Holm, 1999) (Scheme 1) because π^* orbitals are not available to give radical anions. CAHs could add another electron after Cl^- loss and further reactions would ensue.

CCl_4, CH_3CCl_3 and $C_6H_6Cl_6$ (lindane) required less sodium per chlorine lost than halogenated aromatic compounds, especially in the presence of excess water. In anhydrous ammonia, CCl_4, CH_3CCl_3 and lindane required 1.15, 1.2 and 1.1 equivalents of Na per chlorine, respectively, for complete dechlorination. Chloroaromatic compounds required distinctly larger amounts of Na, except for 2, 3-dichlorotoluene and 1, 2, 3, 4-tetrachlorobenzene which both required 1.25 equivalents of Na per chlorine. With a 50 mol excess of water present, the monochloroaromatic compounds (entries 1–3, Table 2) required 2.5 equivalents of Na while the mono-, di-, and trichlorinated phenols consumed 4.5, 4 and 3.3 equivalents of Na per chlorine removed.

3.3. Dechlorination with deficient amounts of sodium

Partially dechlorinated intermediates were not observed when 1, 2-dichlorobenzene, 3, 4-dichlorotoluene, CCl_4 and CH_3CCl_3 were reduced in $NH_{3(L)}$ with a Na deficiency (Table 3) either with or without H_2O present. For example, 3, 4-dichlorotoluene (Eq. (6)) gave only toluene and recovered starting material when treated with Na/NH_3 at Na/substrate ratios of 1, 2 and 3 in the presence of 5 equivalents of water. A sample GC display is shown in Fig. 2. No monochlorotoluenes could be detected.



(6)

Dechlorinations of CCl_4 with 1, 2 and 3.4 equivalents of Na in anhydrous $NH_{4(L)}$ gave only CH_4, recovered CCl_4 and traces of unknown products. The material balances were almost complete. No $CHCl_3$, CH_2Cl_2 or CH_3Cl were detected by GC analysis. Similarly,

Table 3
Products obtained in sodium-deficient reactions in liquid NH_3 at room temperature[a]

Substrate	Na/substrate (mole ratio)	H_2O/substrate (mole ratio)	Products
3, 4-Dichloro-toluene	1	5	82% SM[b], 18% toluene
	2	5	60% SM[b], 40% toluene
	3	5	25% SM[b], 75% toluene
1, 2-Dichloro-benzene	3.5	5	7% SM[b], 93% benzene
CCl_4	1	0	79% CCl_4, 20% CH_4[c]
	2	0	54% CCl_4, 45% CH_4[c]
	3.4	0	33% CCl_4, 64% CH_4[c]
CH_3CCl_3	2	0	38% CH_3CCl_3, 62% CH_3CH_3[d]

[a] Reactions were carried out by Procedure A and work-ups were performed by Method 2. Estimated experimental error ±3%.

[b] SM – starting material.

[c] No traces of $CHCl_3$, CH_2Cl_2 or CH_3Cl were detected.

[d] No traces of CH_3CHCl_2, CH_3CH_2Cl or CH_2CHCl were found.

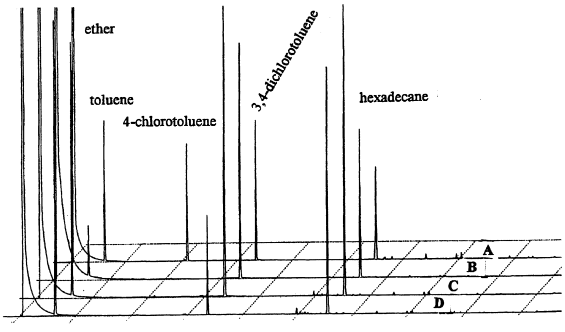


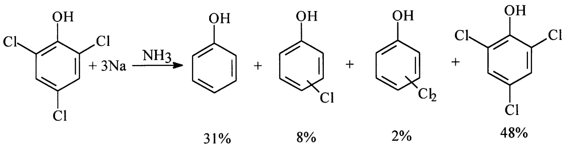
Fig. 2. Graph A – toluene, 4-chlorotoluene, 3,4-dichlorotoluene and hexadecane in Et_2O. Graph B, graph C and graph D – 1/1, 1/2 and 1/3 of Na/substrate (mole ratio) were used, respectively.

dechlorination of CH_3CCl_3 with 2 equivalents of Na produced ethane (62%) and CH_3CCl_3 (38%) was recovered unchanged. The material balances confirm that NH_3 or NH_2^- is not reacting with partially dechlorinated intermediates to give aminated products or elimination.

$$CCl_4 \underset{3.4\ \text{equivalents of Na}}{\overset{Na/NH_3}{\rightarrow}} CH_4 + CCl_4 \tag{7}$$

These results argue that the four dechlorinations in Table 3 are diffusion controlled. Apparently, solvated electrons react rapidly with partially dechlorinated species before these chlorine-containing intermediates can diffuse away to other regions of the solution and be replaced by more substrate. Reaction of solvated electrons with substrate goes to completion faster than substrate escape from the vicinity of the dissolving Na particle, despite rapid stirring. The supply of solvated electrons (Na dissolution) must also be fast enough to completely dechlorinate intermediates before they equilibrate with more substrate in the vicinity of the dissolving particle. Thus, dechlorination appears to be diffusion controlled. Hence, solvated electrons are consumed before mixing can equilibrate them with substrate.

Chlorinated phenols do not react under diffusion control, in contrast to CAHs and chloroaromatic hydrocrbons. When 2,4,6-trichlorophenol was treated with 3 equivalents of Na by Procedure A, small amounts of partially dehalogenated dichlorophenols (2%) and monochlorophenols (8%) were detected (Eq. (8)) showing this reaction is not completely diffusion controlled. One would expect the most highly chlorinated products to always lose chloride faster than partially dechlorinated intermediates. Thus, extremely rapid chlorine loss occurs even though the 2,4,6-trichlorophenoxide anion is the substrate present in NH_3. However, chlorophenoxides dechlorinate slower than CCl_4, CH_3CCl_3 or chlorobenzenes.



(8)

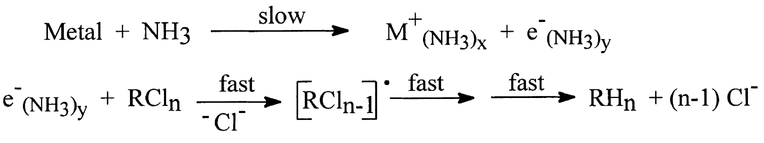
3.4. Effects of Na particle size, mode of addition and temperature. Consumption of solvated electrons in dechlorinations vs reaction with water

The effect of sodium particle size on sodium consumption in 2-chloro-*p*-xylene dechlorination was studied by the use of chunks (>8 mm^3, Procedure A), thin Na mirrors (Procedure C) and preformed solvated electron solutions (Procedure D) in anhydrous $NH_{3(L)}$ and with a 50 mol excess of water (Table 4). Without water, the Na/2-chloro-*p*-xylene ratio required for complete dechlorination was the same for reactions employing chunks and reactions employing mirrors (1.5 equivalents of Na required). A modestly larger Na requirement (1.85 equivalent) was needed when anhydrous, preformed, solvated electron solutions were used. However, in the presence of a 50 mol excess of water, the use of Na chunks led to a substantially lower Na consumption than the use of the thin Na mirror (2.5 vs 4.5 equivalents). Using preformed solvated electron solutions (Procedure D) with a 50 mol excess of water – required a far greater consumption of Na. Only 55% of

Table 4
Effects of Na particle size in halogenation of 2-chloro-*p*-xylene at 25°C

Particle size	H_2O/substrate (mole ratio)	Na/substrate required (mole ratio) for complete dehalogenation[a]
Chunk (>8mm^3)[b]	0/1	1.5
	50/1	2.5
Thin mirror[c]	0/1	1.5
	50/1	4.5
Preformed solvated	0/1	1.85
Electron solution[d]	50/1	5 (55%)[e]

[a] S.D.s were ±3%.
[b] Procedure A was employed.
[c] Procedure C was employed.
[d] Procedure D was employed.
[e] Only 55% of 2-chloro-*p*-xylene was dechlorinated after 5 equivalents of Na had been consumed.



Scheme 2.

the 2-chloro-*p*-xylene was dechlorinated when 5 equivalents of Na had been consumed.

Dechlorination can be discussed in two steps:

1. dissolution of the metal (M) in ammonia to give solvated electrons and
2. reaction of solvated electrons with the substrate (Scheme 2).

Solvated electrons react at a diffusion controlled rate, completely reducing polychlorinated species before intermediates diffuse away, even when a stoichiometric Na deficiency exists. As they form, solvated electrons destroy all the RCl in the volume of solution near the Na. Therefore, water remaining in that volume can react with solvated electrons also remaining in that region once RCl is consumed. The highest dechlorination selectivity (lowest Na consumption per chlorine), would occur at solvated electron production rates which are slow enough to permit RCl to diffuse into this region near the metal surface. This allows the solvated electrons to be consumed rapidly by chloroorganic species rather than by water. Solvated electron generation rates increase with more surface area. Use of larger Na particles will decrease the overall rate of generating solvated electrons. Thus, a lower consumption of Na per mole of chlorine removed should be observed as the Na particle size increases.

A comparison of addition protocols (Procedure A vs Procedure B) found no differences in the amount of Na required to totally dechlorinate 2-chloro-*p*-xylene (Table 5) However, a significant difference in the amount of Na required was observed in chlorooctane dechlorinations upon comparing Procedures A and B in the presence of a 50 mol excess of water. Four equivalents of sodium completely reduced 1-chlorooctane in Procedure B, whereas only 80% of the 1-chlorooctane was reduced with 7 equivalents of sodium in Procedure A. In this specific case, chlorooctane has a low solubility in liquid ammonia solutions containing a high mole fraction of water. Chlorooctane requires several seconds to dissolve completely into solution (H_2O 0.9 g/NH_3 10 ml) with vigorous shaking. Thus, substrate was delivered more slowly to the solvated electrons being formed in Procedure A, thereby allowing water to compete more effectively.

Temperature did not seriously affect the Na consumption required to complete dehalogenation (Table 6) except for 1-chlorooctane and 4-chlorophenol. The Na/substrate ratios required with 2-chloro-*p*-xylene and 3-fluoro-*o*-xylene (Table 6) did not change very much with or without added water at room temperature or at −55°C. The high Na consumption required for chlo-

Table 5
Effect of different modes of addition on sodium consumption

Substrate	H_2O/ substrate (mole ratio)	Na/substrate (mole ratio) required for complete dehalogenation in different procedures	
		Procedure A	Procedure B
2-Chloro-*p*-xylene	0/1	1.5	1.6
	5/1	2.3	2.4
	20/1	2.4	2.5
	50/1	2.5	2.6
n-Chloro-octane	0/1	1.7	1.9
	5/1	2.3	2.3
	20/1	3.5 (97%)[a]	2.5
	50/1	7 (80%)[b]	4.0

[a] Only 97% of *n*-chlorooctane was dechlorinated.
[b] Only 80% of *n*-chlorooctane was dechlorinated at a cost of 7 equivalents of sodium consumption.

Table 6
Effects of temperature in Na/$NH_{3(L)}$ dehalogenations

Substrate	H_2O/ substrate	Na/substrate (mole ratio) required for complete dechlorination[a]	
		25°C	−55°C[b]
2-Chloro-*p*-xylene	0/1	1.5	2.0
	50/1	2.5	3.0
3-Fluoro-*o*-xylene	0/1	2.0	2.0
	50/1	4.0	4.5
4-Chlorophenol	0/1	2.0	2.1
	50/1	4.5	2.5
n-Chlorooctane	0/1	1.7	2.5
	50/1	4.0	5.0 (15%)[c]

[a] S.D. ±3%.
[b] Procedure E used in these experiments.
[c] Only 15% of *n*-chlorooctane was dechlorinated.

Table 7
Activity of different halides in dehalogenation of aromatic halides in Na/NH_3 at 25°C

Substrate	H_2O/substrate (mole ratio)	Na/substrate required for complete dehalogenation		
		F	Cl	Br
2-X-*p*-xylene (X = Br and Cl) or 3-fluoro-*o*-xylene	0/1	2.0	1.5	1.5
	50/1	4.0	2.5	2.5
4-X-phenol (X = F, Cl and Br)	0/1	2.0 (18%)[a]	2.0	2.2
	50/1		4.5	6.0

[a] Only 18% of 4-fluorophenol was defluorinated in 20 hour reaction time.

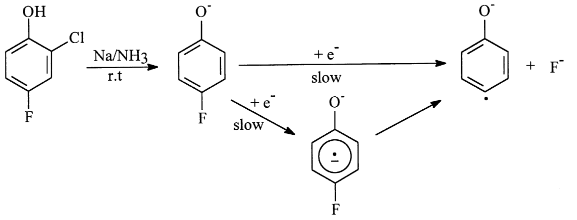
rooctane was related to its poor solubility in aqueous ammonia, especially at −55°C.

Only 2.5 equivalents of Na were required for complete dehalogenation of 4-chlorophenol at −55°C vs 4.5 equivalents to achieve the same result at room temperature. 4-Chlorophenol was soluble (as the phenoxide) in liquid NH_3 at −55°C. However, ice crystals were observed at this low temperature so the water concentration in solution was lower than at room temperature. Substantial amounts of water were frozen at −55°C in all dehalogenations, so it is difficult to assess reasons for the change in Na consumption going from 25°C to −55°C.

3.5. Activity of different halogens and metals in dehalogenations

Since the strength of C–X bonds increases in the order C–I < C–Br < C–Cl < C–F, the reactivity decreases in going from C–I to C–F (Austin et al., 1990). Mackenzie et al. (1986) reported that no obvious halogen-based (X = F, Cl, Br) selectivity was found during reductions of α-halogenated naphthalenes. Reductions of haloxylenes and 4-halophenols were carried out in Na/NH_3 (Table 7) to compare the effect of different halides. In each case, more sodium was required for defluorination than for dechlorination or debromination. This was true with or without added water. This difference was larger in 4-halophenol dehalogenations. Chlorophenol and bromophenol were completely destroyed by 2 and 2.2 equivalents of Na in 30 s at ambient temperature, respectively, with no water present. However, 4-fluorophenol was only 18% defluorinated after 20 h using 2 equivalents of sodium. Adding water increased the Na requirement for all three halides (Table 7).

Fluorophenoxide ions are extremly difficult to defluorinate. Dechlorination of 4-fluoro-2-chlorophenol, with 3 equivalents of sodium, was fast, but after 3 h only 3% defluorination to phenol occurred. 4-Fluorophenol was obtained in 97% yield (Eq. (9)).



(9)

The amount of Li, Na, K and Ca required for complete dechlorination of 2-chloro-*p*-xylene was compared (Table 8). The electrode potentials for loss of a single electron in NH_3 at −55°C are: Li (2.99 V), Na (2.59 V), K (2.73 V) and Ca (2.39 V) (Pleskov, 1937a,b). If dechlorination rates followed the order of the electrode potentials, the expected order of rates would be Li > K > Na > Ca. However, if solvated electrons are transferred at diffusion-controlled rates, the rate of metal dissolution and other factors could play a more important role in processes competiting for those electrons (see discussion on particle size). Sodium gave the lowest stoichiometric consumption of the four metals to complete 2-chloro-*p*-xylene dechlorination, with or without water. In the absence of water, 1.5 equivalents of sodium were required, versus 2, 1.8 and 2 equivalents of lithium, potassium and calcium, respectively. With a 50 mol excess of water, only 2.5 equivalents of Na were

Table 8
Activity of different metals in dehalogenations of 2-chloro-*p*-xylene at 25°C

H_2O/substrate (mole ratio)	Metal/substrate (mole ratio) required for complete dehalogenation[a]			
	Li	Na	K	Ca
0/1	2.0	1.5	1.8	1.0
50/1	6.0 (76%)[b]	2.5	5.7	2.5 (23%)[c]

[a] S.D. ±3.5%.

[b] Seventy-six % of the substrate was dechlorinated.

[c] Twenty-three % of the substrate was dechlorinated.

required, versus 5.7 equivalents potassium to complete dechlorination at those conditions. Lithium and calcium reactions were very inefficient in the presence of water, giving only 76% and 23% dechlorination with 6 and 5 equivalents of metal, respectively. Surface passivation by insoluble hydroxides (LiOH or $Ca(OH)_2$), generated by reaction with water, prevented rapid metal dissolution. Reaction times of about 2 min were required in these cases. Thus, sodium has a substantial advantage over calcium, potassium and lithium in the presence of water and it might be the metal of choice for use in soil/NH_3 slurry remediations.

4. Conclusions

Solvated electrons react at diffusion-controlled rates with CCl_4, CH_3CCl_3 and chlorinated aromatic compounds under the conditions applied. The addition of substantial amounts of water only modestly increased the amount of Na needed to completely dechlorinate organic substrates. These diffusion-controlled reductions were complete in about 30 s, which was the time needed for complete metal dissolution in liquid ammonia. Diffusion control was supported by the absence of partially dechlorinated products in reductions of multiply chlorinated molecules in sodium-deficient partial reductions. Only the chlorinated phenols exhibited minor amounts of partially dechlorinated products in accord with a greater reluctance of the corresponding phenoxides to add an electron.

The blue color of solvated electrons in NH_3 near the surface of the Na disappeared immediately in the presence of chlorinated substrates even at −55°C. Efficient stirring, larger particle size and control of the dissolution rate into $NH_{3(L)}$ lead to the lowest Na consumption in the presence of water. The consumption of sodium was less than that of calcium, potassium and lithium, especially in the presence of water, suggesting sodium is the metal of choice for remediation.

Acknowledgements

Support of this research was provided by the US Environmental Protection Agency, grant no. GAD #R826180 and by the Department of Interior, US Geological Survey, Grant number HQ 96GR02679-12.

References

Aiired, E.L., Beck, B.R., Voorkees, K.J., 1974. J. Org. Chem. 39, 1426.

Austin, E., Alonso, R.A., Rossi, R.A., 1990. J. Chem. Res., 190–191.

Birch, A.J., Subba Rao, G., 1972. Adv. Org. Chem. 8, 33.

Chuang, F.-W., Larson, R.A., Wessman, M.S., 1995. Environ. Sci. Technol. 29, 2460.

Crooks, R.M., Bard, A.I., 1987. J. Phys. Chem. 91 (5), 1274.

Eastham, J.E., Larkin, D.R., 1959. J. Am. Chem. Soc. 81, 3652–3655.

Gould, R.F. (Ed.), 1965. Advances in Chemistry. American Chemical Society, Washington, DC, pp. 50.

Holm, T., 1999. J. Am. Chem. Soc. 121, 515.

Jessup, D.W., Paschal, J.W., Rabideau, P.W., 1977. J. Org. Chem. 42, 2620–2621.

Knorre, H., Langer, M., Pohl, G., 1980. Degussa AG Patent DE 2813200 C2.

Lahaniatis, E.S., Parlar, H., Klein, W., Korte, F., 1975. Chemosphere 2, 83–88.

Liu, Y., Schwartz, J., Cavalloro, C.L., 1995. Environ. Sci. Technol. 29, 836.

Mackenzie, K., Kopinke, F.D., Remmler, M., 1986. Chemosphere 33 (8), 1495–1513.

Pittman Jr., C.U., Mohammed, M.K., 1996. Preprint. Extended Abstracts of the Special ACS Symposium: Emerging Technologies in Hazardous Waste Management VII. Birmingham, AL, 9–11 September, pp. 557–560.

Pittman Jr., C.U., Tabaei, S.M.H., 1994. Unpublished results, Mississippi State University. Presented at the 1994–1995 SAC/IAC Meeting of the Gulf Coast Hazardous Substance Research Center. Beaumont, TX.

Pittman Jr., C.U., Tabaei, S.S.H., 1993. Preprint. In: Tedder, D.W. (Ed.), Extended Abstracts of the Special ACS Symposium: Emerging Technologies in Hazardous Waste Management V, vol. 2. Atlanta, GA, 27–29 September, 1993, pp. 557–560.

Pleskov, V.A., 1937a. Zh. Fiz. Khim. 9, 12.

Pleskov, V.A., 1937b. Acta Physicochim. URSS 6, 1.

Rabideau, P.W., Wetzeland, D.M., Yong, D.M., 1984. J. Org. Chem. 49, 1544–1549.

Schindewolf, U., 1970. In: Lagowski, J.J., Sienko, M.J. (Eds.), Metal–Ammonia Solution. Butterworths, London, pp. 199–218.

Smith, M., 1968. In: Augustine, R.L. (Ed.), Dissolving Metal Reductions, in Reduction: Techniques and Application in Organic Synthesis. Marcei Dekker, New York, pp. 99–170.

Tabaei, S.M.H., Pittman Jr., C.U., 1993a. Hazardous Waste and Hazardous Mater. 10 (4), 431–440.

Tabaei, S.M.H., Pittman Jr., C.U., 1993b. Tetrahedron Lett. 34 (20), 3263–3266.

Tabaei, S.M.H., Pittman Jr., C.U., Mead, K.T., 1992. J. Org. Chem. 57, 6669.

Toxic Substances Control Act, 1976. Public Low, pp. 94–469.

Watt, G.W., 1950. Chem. Rev. 317–379.

Weinberg, N.D.J., Abel, A.E., 1989. US Patent 4 853 040, 1 August.

Weinberg, N.D.J., Abel, A.E., 1992. US Patent 5 110 364, 5 May.

Yang, C.-M., Pittman Jr., C.U., 1996. Hazardous Waste and Hazardous Mater. 13 (4), 445–464.

Yang, C.-M., Pittman Jr., C.U., 1997. Tetrahedron Lett. 38 (37).

Yang, C.-M., Pittman Jr., C.U., 1998a. Synthetic Commun. 28 (3), 517–525.

Yang, C.-M., Pittman Jr., C.U., 1998b. Synthetic Commun. 28 (11), 2027–2041.