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Mediated Approach for the Electrochemical Reduction of Chlorobenzenes in Nonaqueous Media

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The use of a range of mediators for the partial or complete dechlorination of a series of polychlorinated benzenes has been investigated. The dechlorinations were carried out in acetonitrile, and the products were analyzed by gas chromatography-mass spectroscopy (GC-MS). The partial dechlorination using organic mediators was successful and good control of the reaction (*i.e.*, monodechlorination) and good efficiency could be achieved. Some mediators showed poor current efficiencies due to the lower stability of their anion radical in the presence of protons. The monodechlorination of trichlorobenzene with four different mediators showed that the product distribution in terms of initial chlorine removed was little affected by the mediator used. This product distribution has also been investigated for the whole series of polychlorobenzenes. Polydechlorination using a single mediator was tried using biphenyl, anthracene, and dibenzofuran. After passing enough charge to completely dechlorinate trichlorobenzene, few chlorinated benzenes remained in solution and less than the expected amount of benzene was detected. This was explained by non-volatile products undetected by GC-MS. It is suggested that when higher overpotential mediators are used, the reaction shifts to produce higher molecular weight products by radical-radical coupling reactions. Biphenyl might be a convenient mediator for the dechlorination of polychlorobenzene or even polychlorobiphenyl.

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Chlorinated aromatic compounds are environmental pollutants. One of the essential steps in their detoxification is the removal of the chlorine. This can be accomplished by reduction of the chloro-aromatic molecule either chemically with strong reducing agents or electrochemically at an appropriate cathode. The latter approach does not require the handling of reactive chemicals or the use of elevated temperature making it worthy of investigation. At the cathode, several reactions are possible depending on the reaction conditions. The desired reaction involves replacing the chlorine with a hydrogen atom. This occurs with the consumption of two electrons and one proton. In aprotic media, the proton comes from traces of water, the organic solvent, or the quaternary ammonium cations present in the electrolyte.

If there is more than one chlorine attached to an aromatic ring, the removal of each chlorine normally requires its own potential.^{1,2} The removal of the first chlorine occurs at the least negative potential whereas the last one is removed at the most negative potential.³ Savéant *et al.*^{4,5} studied the reaction mechanisms involved in the dehalogenation of organic molecules and found that in most cases the dechlorination occurs via an electron transfer followed by the irreversible loss of chloride. The electron is first transferred to the π^* orbital of the ring and delocalized among the six carbon atoms. It then moves to the σ^* orbital as the carbon-chlorine bond is broken. The electron transfer can be achieved either at the electrode surface (*i.e.*, by direct electrolysis⁶⁻⁸) or away from the electrode using organic mediators such as phenanthridine (mediated electrolysis.⁹⁻¹²) In the mediated case, the rate at which the electron-transfer occurs depends on the potential difference between the reduced form of the mediator and the dechlorination potential of the reactant molecule.¹³

Generally, an advantage of using mediators is that the cathode is not directly involved in the reduction step, and hence poisoning of its surface is less likely to occur.¹⁴ The use of mediators also allows the electrolysis to be carried out at a less negative electrode potential, leading to a higher reaction current efficiency. This is particularly important for the dechlorination of monochlorobenzene where direct electrolysis is known to show poor current efficiencies due to electrolyte breakdown. Minimizing the electrolyte breakdown also lowers the possibility of filming of the cathode and the subsequent interference of the electrolytic process.¹⁴

In this work, the effects of several mediators are tested on different polychlorobenzenes. The mediators are selected according to

their ability to reduce the polychlorobenzenes and their stability in the electrolytic solution. The selectivity of the reduction is also investigated for the different chlorobenzenes. The controlled cleavage of a single chlorine from the molecule can be of interest for synthesis reactions.

Polydechlorination has also been investigated with mediators that can react to remove more than the first chlorine. The aim is to find a single mediator capable of dechlorinating hexachlorobenzene all the way to benzene in an efficient, clean fashion.

Experimental

Chemicals.—The reactants were obtained from Ingram and Bell Scientific and Aldrich Chemical and were usually used as received. Acetonitrile distilled in glass (Anachemia) was used as received. Tetraethylammonium tetrafluoroborate (TEABF₄) was recrystallized from water/ethanol solution and dried at 60°C for 3 days. Tetraethylammonium bromide (TEAB) was used as received from the manufacturer.

Electrodes.—Glassy carbon was usually used as the cathode material. For cyclic voltammetry experiments, a disk electrode was fabricated from a glassy carbon rod (diameter 3 mm) and pressed into a Teflon holder. For the electrolysis experiments the cathode was a glassy carbon plate (thickness ~2 mm) with working dimensions 15 × 30 mm. A magnesium rod was used as counter electrode in the electrolysis experiments and a Pt foil in cyclic voltammetry experiments. The reference electrode in all experiments was Ag/0.1 M AgNO₃ in CH₃CN and all potentials are referred to it in this work. For a solution of 1 mM ferrocene, the formal potential is +0.03 V vs. Ag/0.1 M AgNO₃.

Voltammetry.—Cyclic voltammetry curves were obtained with a EG&G potentiostat, model 363, connected to a universal programmer, EG&G model 175. The experiments were performed at room temperature; 40 mL of solution was placed in a conical cell, and argon was used to deoxygenate the solution prior to each scan.

Electrolysis.—Electrolysis experiments were performed using an H-type cell. The cell was either undivided (60 mL) or divided with a glass frit (53 mL working and 7 mL counter compartment). The side of the H-type cell with the cathode was continuously purged with argon and stirred with a magnetic stirrer sealed in a glass tube. The electrolyses were performed in a galvanostatic mode and the current was set to well below the mass transport limit of the mediator. The potential of the working electrode, which was monitored vs. the sil-

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Figure 1. Cyclic voltammogram of hexachlorobenzene at a glassy carbon electrode. Electrolyte: 0.1 M TEABF₄ in acetonitrile. Sweep rate: 50 mV/s.

ver nitrate reference electrode, remained close to the reduction potential of the mediator until the end of the electrolysis. The extent of the dechlorination reaction was monitored by gas chromatography (0.5 mL samples were withdrawn from the cathode compartment in a regular manner for analysis).

Analytical procedures.—GC-MS was run using a Hewlett Packard GCD Series gas chromatograph (model G1800A) with electron ionization detector. A HP-5 capillary column (30 m, 0.25 mm diam, 0.25 μ m of 5% polyphenylmethylsiloxane coating) from Hewlett-Packard was used for the separation. For quantitative analysis, a known amount of toluene and/or methoxyacetophenone was added to the samples before they were run by GC-MS. Usually 0.5 mL samples were mixed with 1 mL of this internal standard solution with 0.5 μ L injected at a 25:1 split ratio. In general, the temperature of the column was held at 40°C for 5 min then ramped to 250°C in 21 min and held there for another 5 min. The final temperature was raised to 300°C to check for high-boiling compounds that could be generated by coupling side reactions. When only higher-boiling compounds were expected (such as polychlorinated benzenes), the initial temperature was 80°C to speed up the analysis.

The injector was always maintained at a temperature of 210°C and the inlet of the MS was maintained 30°C higher than the final temperature of the column.

Results and Discussion

Direct electrochemistry.—The reduction of polychlorinated benzene in aprotic media occurs in a stepwise manner, the elimination of each subsequent chlorine requiring a more negative potential.¹⁻³ Figure 1 shows the reduction of hexachlorobenzene in acetonitrile at a glassy carbon electrode. Each peak indicates the loss of one chlorine. The loss of the last chlorine occurs with the onset of solvent breakdown.

For electrosynthesis, it may be necessary to control the reduction of polychlorinated benzene so that only one chlorine is removed. The first approach taken was to carry out direct electrolysis without any mediator present in the solution. 1,2,3-Trichlorobenzene was chosen as a model compound for this part of the study. The electrolysis of 1,2,3-trichlorobenzene (5 mM) was conducted in a 0.1 M TEAB in acetonitrile solution. The current was set so that the potential of the glassy carbon cathode remained close to -2.6 V where the cleavage of the first chlorine occurs (see Fig. 1). After enough charge was passed to theoretically reduce all the trichlorobenzene to dichlorobenzene, 22% of the trichlorobenzene was found to be unreacted whereas only 65% had been converted to dichlorobenzene. As the reduction continued, small quantities of chlorobenzene were generated. The selectivity for the dichlorobenzenes obtained (after reacting 80% of the trichlorobenzene) was: 63% 1,3-dichlorobenzene and 37% 1,2-dichlorobenzene. The same experiment was repeated with four other cathode materials (*i.e.*, mercury, lead, iron, and platinum). The product distributions are reported in Table I. It is seen that the product distribution is only slightly influenced by the cathode material. However, the current efficiency seems to be different for the different materials; this is presumably due to the influence of electrode material on catalytic properties.⁶ In general, a glassy carbon cathode is believed to have fewer interactions with organic molecules since it does not form organometallic intermediates as is found with, for example, mercury.¹⁵ Consequently, glassy carbon is a convenient electrode material to use in the present investigation.

Mediated dechlorination.—In a previous paper, the dechlorination of monochlorobenzene using organic mediators was discussed.¹⁴ The use of mediators to dechlorinate monochlorobenzene was found advantageous as it allows the electrolysis to be operated at less negative potentials where solvent breakdown is not a concern. The mediated approach is now investigated for polychlorinated benzenes and the results are compared to those for the direct electrolysis method.

In order to choose a good mediator for the monodechlorination of polychlorinated benzene, it is important to consider the rate of reaction of this mediator with respect to the reactant and the products. The rate of electron transfer between the mediator and the substrate is primarily a function of the difference in standard potentials between the two. The larger the difference, the faster is the rate of elec-

Table I. Product distribution for the direct reduction of 1,2,3-trichlorobenzene (≈ 8.5 mM) at different cathode materials. The current was adjusted so that only the first chlorine was removed.

Cathode material	I_{eff} for dichlorobenzene formation	Fraction of trichlorobenzene unreacted	Fraction of dichlorobenzene	Fraction of chlorobenzene and benzene	Isomers	
					% 1,3	% 1,2
Glassy carbon	0.63	0.22	0.65	0.00	63	37
Iron	0.86	0.06	0.87	0.06	65	35
Lead	0.79	0.15	0.82	0.00	75	25
Mercury	0.98	0.38	0.68	0.00	70	30
Platinum	0.73	0.18	0.76	0.00	70	30

Electrolyte solution: 0.1 M TEAB in acetonitrile. Anode: Mg.

Fraction: represents the ratio of a certain compound over the amount of trichlorobenzene introduced in the solution.

tron transfer. Each polychlorinated benzene can potentially react with a given mediator. Therefore, a mediator with a too negative reduction potential might also interact with the initial dechlorination product and further dechlorinate it. It is therefore important to choose a mediator which has a reduction potential sufficiently negative to remove quickly the first chlorine, but not so negative that it has an effect on the further dechlorination reactions. Each chlorine loss is separated by about 200 to 250 mV (Fig. 1). This allows for a significantly different rate of reaction between the mediator and the different chlorobenzenes.

Dechlorination of 1,2,3-trichlorobenzene.—Phenanthridine was found to be the most convenient mediator for the removal of the first chlorine from 1,2,3-trichlorobenzene. A typical voltammogram of phenanthridine in the absence of trichlorobenzene shows a reduction and an oxidation peak (Fig. 2). This indicates that phenanthridine forms a relatively stable anion radical that can be reoxidized to phenanthridine. Due to the high resistivity of the solution, the difference in peak potentials of 59 mV, generally characteristic of a reversible one-electron reaction, cannot be measured here. Nevertheless, the peak height is proportional to the square root of the scan rate and the cathodic peak current is about equal to the anodic peak current. When 1,2,3-trichlorobenzene is added to a solution containing phenanthridine, the reduction peak of the latter increases and the oxidation peak of the anion radical eventually disappears (Fig. 2). This indicates that the overall process becomes irreversible, suggesting a subsequent chemical reaction involving the anion radical and resulting in the regeneration of the parent (mediator) molecule.

The rate constant for homogeneous electron transfer can be measured by linear sweep voltammetry techniques according to the method suggested by Savéant¹⁶ for the catalytic current. This method has already been described in an earlier paper.¹⁴ The result thus obtained for trichlorobenzene with phenanthridine as mediator is $\log k_{3 \rightarrow 2} = 4.3$. This rate of reaction is calculated assuming that trichlorobenzene is reduced via a two-electron transfer to dichlorobenzene and that the further reduction of dichlorobenzene can be neglected. For the reaction between phenanthridine and 1,2-dichlorobenzene, we found $\log k_{2 \rightarrow 1} = 1.5$. This rate constant is about 600 times smaller than that for 1,2,3-trichlorobenzene, *i.e.*, small enough so that further reduction to monochlorobenzene can be neglected.

Three other mediators with similar reduction potentials were also tested for the dechlorination of 1,2,3-trichlorobenzene. The rate constants were determined using the same method as for phenanthridine and given in Table II. It is seen that slightly smaller rate constants result when acetophenone and anthracene are used as mediators instead of phenanthridine and 2-methoxyacetophenone. This difference in rate constant is small, and it should not make any significant difference in their capabilities to reduce trichlorobenzene. Also, the

Table II. Rate constants for homogeneous electron transfer.

Mediator	ΔE_p (V)	Log k
2-methoxyacetophenone	0.14	4.3
Phenanthridine	0.16	4.3
Acetophenone	0.21	3.7
Anthracene	0.24	3.8

k : rate constant for homogeneous electron transfer measured by linear sweep voltammetry techniques.¹⁴

ΔE_p is the peak potential difference between mediator and 1,2,3-trichlorobenzene measured at a 50 mV/s scan rate for a concentration of 1 mM.

rate constants are generally in agreement with literature values which predict that the mediator with the least negative potential has a slower rate of electron transfer with the reactant.¹³

The direct electrolysis of 1,2,3-trichlorobenzene (5 mM) at 10 mA in the presence of phenanthridine (2 mM) was performed for 100 min. The cathode potential remained almost constant at the reduction potential of the mediator. Towards the end of the electrolysis, the potential slowly began to shift to more negative values. The mass balance was fairly well maintained during the experiment (Fig. 3). After 95% of the trichlorobenzene was reacted (100 min of electrolysis), the sum of total benzenes only dropped by 10%. The only two detected products were 1,2-dichlorobenzene and 1,3-dichlorobenzene, and their ratio stayed constant (32:68) throughout the electrolysis. Neither monochlorobenzene nor benzene was detected by GCMS after the passage of 60 C of charge. The current efficiency obtained was about 80%. These results show that phenanthridine is an appropriate mediator and that the difference in rates of reaction of the mediator with 1,2,3-trichlorobenzene and dichlorobenzenes are sufficiently large that only the first reaction occurs. Obviously, the selective removal of the first chlorine from 1,2,3-trichlorobenzene can be successfully achieved with phenanthridine as a mediator.

The electrolysis described above was repeated with the three other mediators listed in Table II. The product distributions and current efficiency were determined for each electrolysis and are reported in Table III. The selectivity does not change significantly when acetophenone or 2-methoxyacetophenone is substituted for phenan-

Figure 2. Cyclic voltammogram of anthracene and 1,2,3-trichlorobenzene in 0.1 M TEAB solution of acetonitrile. Sweep rate: 400 mV/s.

Figure 3. Electrolysis of 1,2,3-trichlorobenzene (5 mM) in the presence of phenanthridine (2 mM) at a glassy carbon cathode (area 5 cm²) and a magnesium anode. Electrolyte solution: 0.1 M TEAB in acetonitrile. Galvanostatic: $I = 10$ mA.

Table III. Product distribution for the reduction of 1,2,3-trichlorobenzene (5 mM) using various mediators (2.5 mM). Electrolyte solution: 0.1 M TEAB in acetonitrile. Galvanostatic: $I = 10$ mA. For the electrolysis without mediator, the current was reduced from 10 to 7.5 and then to 5 mA as the concentration of substrate decreased.

Mediator	I_{eff} for dichlorobenzene formation	Fraction of trichlorobenzene unreacted	Fraction of dichlorobenzene	Fraction of chlorobenzene and benzene	Isomers	
					% 1,3	% 1,2
Anthracene	0.71	0.21	0.71	0.00	76	24
Acetophenone	0.62	0.29	0.62	0.00	68	32
2-Methoxyacetophenone	0.62	0.26	0.62	0.00	67	33
Phenanthridine	0.82	0.13	0.82	0.00	66	34
No mediator	0.63	0.22	0.65	0.00	63	37

thridine. However, when anthracene is substituted for phenanthridine, the ratio of 1,3-dichlorobenzene to 1,2-dichlorobenzene increases by several percent. This difference cannot be easily explained. Usually the first electron transfer between aromatic organic mediators and halogenated compounds is described as a homogeneous electron transfer.¹⁷⁻¹⁹ The nature of the mediator should therefore not affect the selectivity of the subsequent chemical reaction taking place. Thus the reaction with anthracene might not be completely outer sphere.

Due to traces of water present in the electrolyte solution, poorer current efficiencies (of ~60%) were found when acetophenone or 2-methoxyacetophenone was used as mediator. These two mediators are more reactive with small amounts of water in the solution,²⁰ and both mediators were consumed during the electrolysis. It is likely that the ketone group gives a less stable anion radical in the presence of a proton donor. Nevertheless, the mass balance and selectivity for the trichlorobenzene reduction did not seem to be affected by this side reaction of the mediator. The presence of water decreases the stability of the mediator anion radical intermediate but it also minimizes the destruction of the salt electrolyte, which can also serve as a source of protons necessary for the dechlorination reaction. Some electrolyses were carried out with small amounts of water added to the electrolyte. The current efficiencies for the reaction decreased as the water content is increased, though the selectivity of the reduction of trichlorobenzene stayed unchanged. The addition of small amounts of water can be useful for minimizing the extent of salt destruction if a lower current efficiency is not too critical.

In order to test the effect of the divided vs. undivided cell configuration, the electrolyses of 1,2,3-trichlorobenzene using acetophenone, anthracene, 2-methoxyacetophenone, and phenanthridine was performed using a cell without a frit to separate the cathode from the anode compartment. For all mediators, the current efficiency decreased by less than 10%. The selectivity of the mediated reduction of 1,2,3-trichlorobenzene was not affected by the undivided configuration of the cell. It appears that the cell configuration does not have any significant effect on the reaction mechanism and rate. This result is consistent with each reaction (*i.e.*, the reduction of trichlorobenzene and the generation of Mg^{2+}) taking place in close proximity to their respective electrodes and immediately forming an

“inert” product [dichlorobenzene and a precipitate of MgCl_2 and/or $\text{Mg}(\text{OH})_2$]. The main disadvantage of the undivided cell design is that MgCl_2 and/or $\text{Mg}(\text{OH})_2$ precipitate, thus eventually affecting the stirring of the solution. For this reason, the divided cell design is usually preferred over the undivided one.

Mediated electrolysis of 1,2,4-trichlorobenzene.—Electrolysis experiments were carried out with 1,2,4-trichlorobenzene as substrate. The potential of reduction of 1,2,4-trichlorobenzene is very similar to that of 1,2,3-trichlorobenzene (≈ 50 mV more negative). Therefore, the same mediators can be used for the dechlorination of these two compounds. It is therefore not surprising that similar current efficiencies and mass balances were found for the mediated electrolysis of the two. Only a very small amount of monochlorobenzene and no benzene were generated during the electrolysis of 1,2,4-trichlorobenzene showing that the mediators had good selectivity for the monodechlorination. The results of the electrolysis experiments with different mediators are reported in Table IV. The results indicate that the product distribution is basically independent of the mediator used. This is in agreement with an outer-sphere electron transfer, as usually described in the literature for this type of reaction.¹⁷⁻¹⁹ Direct electrolysis is also reported in the table, and the distribution of dichlorobenzenes does not show any significant difference when compared with the mediated approach. Only a poorer current efficiency is noted in the former.

Product distribution for the series of chlorinated benzenes.—All chlorinated benzenes can be reduced using the mediated approach. Many organic mediators have been reported in the literature for their ability to reduce halogenated molecules.^{9-12,21-22} From the literature, a number of mediators were selected according to their reduction potential and their stability in the electrolyte in the anion radical form. In general, aromatic compounds with a reversible reduction potential 150 to 250 mV less negative than the reduction peak potential of the polychlorobenzenes being studied are a good starting point in the selection of a mediator. The selected mediators were then tested for the dechlorination of different polychlorinated benzenes. The rate of electron transfer was measured by voltammetry (as described previously¹⁴). The successful mediators had to show a good ability in reducing the polychlorobenzene ($\log k > 3$) but at the

Table IV. Product distribution for the reduction of 1,2,4-trichlorobenzene with various mediators. Electrolyte solution: 0.1 M TEAB in acetonitrile. Galvanostatic: $I = 10$ mA. For the electrolysis without any mediator, the current was reduced from 10 to 7.5 then to 5 mA as the concentration of substrate decreased.

Mediator	I_{eff} for dichlorobenzene formation	Fraction of trichlorobenzene unreacted	Fraction of dichlorobenzene	Fraction of chlorobenzene and benzene	Isomers		
					% 1,4	% 1,3	% 1,2
Phenanthridine	0.62	0.14	0.62	0.002	88	10	2
Anthracene	0.51	0.30	0.51	0.002	88	10	2
Acetophenone	0.60	0.31	0.60	0.003	87	10	2
2-Methoxyacetophenone	0.59	0.30	0.59	0.004	87	11	2
No mediator	0.43	0.41	0.43	0.008	86	11	3

Table V. Mediated removal of a single chlorine from polychlorinated benzenes.

Reactant ^a	Mediator	Voltammetry		Electrolysis		
		ΔE_p (V)	Log k	Fraction unreacted	Fraction products	Current density (mA)
1	Biphenyl	0.17	4.0	0.00	0.99	12
1, 2	Benzonitrile	0.22	3.9	0.01	0.91	10
1, 3	Benzonitrile	0.22	3.8	0.07	0.74	10
1, 2, 3	Phenanthridine	0.19	4.3	0.13	0.82	10
1, 2, 4	Phenanthridine	0.20	4.0	0.14	0.62	10
1, 2, 3, 4	Benzophenone	0.24	3.5	0.00	0.98	7
1, 2, 3, 5	Benzophenone	0.26	3.2	0.01	0.82	7
1, 2, 3, 4, 5	Diethylphthalate	0.18	3.6	0.02	0.86	7

^a Position of the chlorines on the benzene molecule.

Electrolyte solution: 0.1 M TEAB in acetonitrile.

Voltammetry: at a glassy carbon disk electrode (diam 3 mm). The rate constant (k) for homogeneous electron transfer measured by linear sweep voltammetry techniques.¹⁴Electrolysis: at a glassy carbon cathode $1.5 \times 3.0 \text{ cm}^2$. Reactant: 5 mM. Mediator: 2.5 mM. For tetrachlorobenzene studies, the mediator concentration was increased to 10 mM. The fraction of products corresponds to the ratio of amount of reactant where a single chlorine has been removed over the initial amount of reactant.

same time had to show a slow rate of reaction with the initial dechlorination products so that the reaction would not proceed beyond removal of the first chlorine. Water was also a concern, as the rate of reaction of the reduced form of the mediator with traces of water (or a proton donor in general) was considered a parasitic reaction and was therefore to be avoided. The mediators that showed good abilities in these regards are listed in Table V. Their rate constants for homogeneous electron transfer and ΔE (difference in peak potentials) were determined by voltammetry. In the same table, the results from the preparative electrolyses are also reported. These electrolyses show a good mass balance and current efficiency. The total benzenes detected was quite good (≈ 70 -100%). It was also possible to obtain a high rate of cleavage of a single chlorine from the polychlorinated benzene without having any removal of a second chlorine. Only small quantities of multiply dechlorinated chlorobenzenes were detected (always less than 3% of total benzenes). The control of the reaction was very good. It is therefore possible to select a mediator that can selectively remove a single chlorine at a reasonable rate from a polychlorinated benzene and still achieve a high

yield and current efficiency. The product distribution obtained for these various polychlorinated benzenes is reported in Table VI.

These results are compared to other studies^{2,3} that used the direct approach to electrolyze chlorobenzenes. The main differences between these three sets of experiments are the product distribution obtained when reducing 1,2,3-trichlorobenzene or 1,2,3,5-tetrachlorobenzene. These differences imply that different reaction mechanisms are involved. This is not unexpected as different electrode materials and conditions are used for these three sets of experiments. Mercury electrodes are well known for their tendency to involve organometallic intermediates. In the present study, the electron transfer occurs away from the electrode and is certainly outer sphere, which corresponds to the case where the electrode and the mediator have the least effect on the selectivity of the cleavage of chlorine. Previous studies have tried to correlate the experimental result of chlorine cleavage with quantum calculations.^{23,24} These types of calculation assume that there are no interactions between the molecule and its environment. Semiempirical calculations have been tried with little success at a complete prediction of the observed experimental re-

Table VI. Product distribution for the series of polychlorinated benzenes.

Reactant ^a	Mediator	Product position of the chlorines	Statistical distribution	Distribution % (This work)	Distribution % (Ref. 3)	Distribution % (Ref. 2)
1, 2, 3	Phenanthridine	1, 3	1	66	40	100
		1, 2	2	34	60	0
1, 2, 4	Phenanthridine	1, 4	1	88	57	84
		1, 3	1	10	21	12
		1, 2	1	2	22	4
1, 2, 3, 4	Benzophenone	1, 2, 4	2	98	99	96
		1, 2, 3	2	2	1	4
1, 2, 3, 5	Benzophenone	1, 2, 4	1	78	91	
		1, 3, 5	1	22	9	
		1, 2, 3	1	0.1	0	
1, 2, 3, 4, 5	Diethylphthalate	1, 2, 3, 5	2	74	65	
		1, 2, 4, 5	1	25	21	
		1, 2, 3, 4	2	1	14	

Electrolyte solution: 0.1 M TEAB in acetonitrile.

^a Position of the chlorines on the benzene molecule.

Ref 3: direct electrolysis at a mercury cathode in DMSO.

Ref 2: direct electrolysis at a reticulated vitreous carbon in DMF.

Figure 4. Electrolysis of 1,2,4-trichlorobenzene (3 mM) in the presence of biphenyl (20 mM) at a glassy carbon cathode (area 5 cm²) and a magnesium anode. Electrolyte solution: 0.1 M TEAB in acetonitrile. Galvanostatic: $I = 25$ mA.

sults.²⁵ These algorithms are certainly too simple to be able to model the complicated experimental system that constitutes these polychlorinated benzenes and do not give sufficient accuracy to predict the rate of cleavage of the different chlorines. Predicting which chlorine will be removed first requires correctly evaluating the effect of the substituents on the electron density of the chlorobenzene anion radical and on the transfer of the electron from the π^* to σ^* orbital which leads to the C–Cl bond cleavage. Some authors suggest this forbidden transition is possible via an out-of-plane vibration of the C–Cl bond^{5,26} that allows the two orbitals to become more in line. If so, the probability of a given transition and bond cleavage would be effected by electron density of the polychlorobenzene anion radical at the associated carbon and by the ease of the C–Cl out-of-plane vibration, both which would be affected by the neighboring substituents. Such calculations would require significant computation effort and are beyond the scope of the present investigation.

Cleavage of more than one chlorine at the same time.—Removing a single chlorine from polychlorinated benzenes is only advantageous for synthesis purposes. For detoxification of polychlorinated benzenes, it is preferable that all the chlorines are removed from the molecule, since this makes further treatment of the toxin considerably easier or possibly allows recycling of the chemicals. Using a

different mediator for each stage of the dechlorination process does not appear to be practical. Another solution is to use a single mediator for removing more than one chlorine on the molecule. The slowest rate of electron transfer for a given mediator is always with the monochlorobenzene molecule, which has the most negative reduction potential. The required mediator for such an experiment therefore has to be able to remove the last chlorine at a reasonable rate.

To reduce trichlorobenzene to benzene, the mediator also has to be able to reduce dichlorobenzene and chlorobenzene. From Table V, it can be seen that biphenyl is a convenient mediator for the reduction of chlorobenzene. Also, the cyclic voltammetry of biphenyl exhibits a reversible peak even at somewhat low scan rates indicating that biphenyl radical anions are stable and react only slowly with the traces of water or other proton donors present in the solution. However, biphenyl reduces at a more negative potential than that required for either dichlorobenzene or trichlorobenzene (≈ 50 mV and ≈ 300 mV, respectively). Direct electrolysis of trichlorobenzene and dichlorobenzene is therefore likely to occur before biphenyl starts to mediate the reductions. In order to avoid direct electrolysis, the concentration of mediator and the applied current density was increased so that the rate of production of the anion radical intermediate is at least four times larger than the rate of mass transport of trichlorobenzene. Under such conditions, trichlorobenzene should not reach the surface of the electrode without being previously reduced by biphenyl radical anions.

The electrolysis resulted in a rapid decrease of trichlorobenzene concentration and the generation of some benzene and chlorobenzene (Fig. 4). No dichlorobenzene was detected during the experiment. Benzene is generated from the beginning of the reaction in larger quantities than chlorobenzene. These results, together with other experiments carried out using phenanthridine as mediator, are combined in Table VII. They show that, when biphenyl is present, benzene is the main product detected, whereas when phenanthridine is used, it is dichlorobenzene. The other major difference between the two sets of experiments is the total mass balance of benzenes, *i.e.*, only $\sim 40\%$ of benzenes are accounted for when biphenyl is used as mediator, whereas more than $\sim 80\%$ of benzenes are accounted for when phenanthridine is used. The $\sim 20\%$ of unaccounted-for benzenes for the later experiments can be attributed to uncertainties in the analysis, possible evaporation caused by deoxygenating with argon and possibly to minor side reaction. A loss of $\sim 60\%$ of total accounted-for benzenes when biphenyl was used as mediator is more significant and requires more attention. Also to account for all the trichlorobenzene reacted, the charge passed was less than that necessary for a two-electron process per chlorine (*i.e.*, six electrons per trichlorobenzene).

In order to explain the poor mass balance of benzenes, it is suggested that as the chlorines are being cleaved from the molecule, the

Table VII. Cleavage of two or more chlorines from polychlorinated benzenes. Electrolysis of (2.5 mM) reactant with mediator in 0.1 M TEAB solution of acetonitrile.

Reactant	Mediator	Med/Re (mM/mM)	Current (mA)	Equiv/mol reactant	Fraction					Sum fractions
					TetrCB	TCB	DCB	CB	Benzene	
1,2	Benzonitrile	2.5/5	5	2	X	X	0.01	0.90	0.00	0.91
1,3	Benzonitrile	2.5/5	5	2	X	X	0.07	0.74	0.00	0.81
1,2	Biphenyl	100/8	70	3.6	X	X	0.32	0.05	0.04	0.40
1,3	Biphenyl	100/8	70	3.6	X	X	0.27	0.03	0.05	0.34
1,4	Biphenyl	100/10	70	3.6	X	X	0.54	0.11	0.09	0.74
1,2,3	Phenanthridine	2.5/5	10	2	X	0.13	0.82	0.00	0.00	0.95
1,2,4	Phenanthridine	2.5/5	10	2	X	0.14	0.62	0.00	0.00	0.76
1,2,3	Phenanthridine	100/5	20	2	X	0.29	0.55	0.00	0.00	0.84
1,2,4	Phenanthridine	20/3.5	25	2	X	0.38	0.42	0.00	0.00	0.80
1,2,3	Biphenyl	20/2.5	25	5	X	0.09	0.00	0.06	0.35	0.49
1,2,4	Biphenyl	20/5	40	5	X	0.08	0.00	0.00	0.21	0.29
1,2,3	Dibenzofuran	100/5	40	5	X	0.11	0.00	0.03	0.24	0.37
1,2,3	Dibenzofuran	20/3.5	25	5	X	0.06	0.00	0.07	0.30	0.43
1,2,3,5	Benzophenone	10/5	7	2	0.01	0.82	0.00	0.00	0.00	0.83
1,2,3,5	Anthracene	10/4	15	3.7	0.08	0.17	0.11	0.00	0.00	0.36

chlorobenzene radicals can dimerize and produce chlorobiphenyls, which could then react further. This is shown in Scheme I, where steps 1-3 are from the literature^{1,2,4,5,13} and step 4 can be expected when radicals are generated. Generally, the rate constants k_2 and k_3 are very fast, and the limiting factor is expected to be the rate of mass transport of the different species. The rate of reaction 2 is usually much slower and can be correlated to the potential difference between the mediator and the chloro-organic species.⁴ From this, it is possible to predict that as the rate constant k_1 increases, the concentration of mediator anion radical tends to decrease whereas the concentration of the dichlorobenzene radical tends to increase. The selectivity of pathway 3 over pathway 4 will then shift to favor the dimerization reaction. Therefore, according to Scheme I, it is possible to predict that reaction pathway 4 will be favored over reaction pathway 3 as the potential of reduction of the mediator becomes more negative. By changing the mediator from phenanthridine to biphenyl, it is equivalent to increasing the rate constant k_1 by several orders of magnitude, for which Scheme I would predict a decrease in pathway 3 leading to a decrease in the formation of benzene and chlorobenzene and an increase in dimers. Experimental results show partial agreement with this prediction as the amount of benzenes recovered decreases as one goes from phenanthridine to biphenyl.

However, work to detect polychlorobiphenyls by GC-MS analysis (to confirm pathway 4) was unsuccessful. This does not, however, invalidate the suggested reduction pathway 4 described in Scheme I. This is because polychlorobiphenyls reduce at potentials that are at least 200 mV less negative than biphenyl.²⁷ Their rate of reaction is therefore expected to be faster or at least as fast as the rate of reduction of the isomers of dichlorobenzene which were also not detected by GC-MS analysis. It can thus be assumed that if tetrachlorobiphenyls are being generated, they should quickly be reduced to form eventually biphenyl or to undergo further radical-radical coupling. The possibility of the formation of biphenyl could not be determined when biphenyl was used as mediator due to its large background concentration.

To investigate this, the mediator biphenyl was replaced by dibenzofuran, which is also a convenient mediator for the reduction of chlorobenzene to benzene.¹⁴ The reduction of trichlorobenzene with dibenzofuran as mediator gives very similar results to those obtained with biphenyl as mediator. Here again, the trichlorobenzene concentration decreases rapidly and a large portion of the benzenes disappears. GC-MS analysis did not detect any biphenyl nor chlorobiphenyls. This result indicates that if tetrachlorobiphenyls are being generated during the electrolysis of trichlorobenzene, they are rapidly reacting to form a molecule with a higher molecular weight than

are not sufficiently volatile to be detected by GC-MS analysis. This might be expected based on the previous discussion.

The potential of reduction for polychlorobiphenyls is usually significantly less negative than polychlorobenzenes.²⁷ From this, the rate constant k_1 is expected to be larger for the polychlorobiphenyls than for the polychlorobenzenes and according to Scheme I, the ratio of radical coupling vs. further reduction of the radical will be higher. The more the radical-radical coupling occurs, the less volatile the molecule becomes and the less likely that it would be detected by GC-MS.

Other reactions were also considered to explain the loss of benzene. Savéant found that there is a possible addition reaction taking place between certain pairs of substrate and mediator.²⁸ GC-MS analysis indicated that small amounts of mediator were being reduced irreversibly. As an example, some biphenyl was reduced to phenyl cyclohexadiene. It is therefore possible to assume that the radical-radical reaction pathway 6 (Scheme II) can also take place. Here again, the molecules so formed can be easily reduced further leading to the eventual complete loss of all chlorines. Unfortunately, GC-MS analysis did not detect any products that could confirm that such reactions are taking place.

From the above, it is impossible to explain conclusively the loss of benzenes during this type of reaction. It can be speculated that some sort of oligomer formation is taking place forming some molecules that are not detected by GC-MS.

A set of experiments was also carried out with dichlorobenzenes as the reactant (see Table VII). Mediated electrolysis of dichlorobenzene produced a small quantity of benzene and chlorobenzene, but not enough to account for all the dichlorobenzene that reacted. Traces of terphenyls were detected by GC-MS. The quantities detected were too small to explain all the unaccounted-for benzenes. Nevertheless, it was an indication that heavier molecules can be formed.

1,2,3,5-Tetrachlorobenzene was reduced in the presence of anthracene as mediator. As expected, some dichlorobenzene was generated as well as some trichlorobenzene. Unfortunately, as with the previous experiments using a single mediator to remove more than one chlorine, the mass balance for the benzenes was very poor (see Table VII). Only 36% of the benzenes were accounted for after reacting more than 90% of the tetrachlorobenzene. These results confirm that the use of a mediator with a potential of reduction far more negative than that of the substrate leads to products that are not detected by GC-MS.

Dechlorination of PCBs.—Some trials were also made on the dechlorination of an industrial PCB mixture (Arochlor 1260) with biphenyl as mediator. These showed that it is possible to react all the

Scheme I. Suggested reduction pathways for trichlorobenzene.

Scheme II. Reaction with the mediator.

polychlorobiphenyls with good current efficiency (assuming $2e^-$ per chlorine). At the end of such electrolysis, GC-MS only detected biphenyl and some reduced products from biphenyl. Using biphenyl as a mediator has the advantage that it is also one of the products from the dehalogenation reaction, thus ensuring a steady supply of mediator and making later product separations simpler.

Conclusions

The results indicate that the use of organic molecules as mediators for reduction of polychlorobenzene is very efficient. It is also possible to control the reaction so that only one chlorine is removed. High current efficiencies and reaction yields can be achieved. The nature of the mediator has little or no effect on the selectivity of the chlorine removal. The preferred mediator has a peak potential less negative than that of the chlorinated benzene substrate and should also have a slow rate of reaction with the traces of proton donors usually present in solution.

In order to simultaneously remove more than one chlorine, the mediated approach becomes more complex. In this case, the successful mediator must also work efficiently on the last chlorine that needs to be removed. Biphenyl is a convenient mediator for complete dechlorination to benzene. Unfortunately, unlike the previous types of dechlorination, the yield of the reaction is very poor and side reactions become a major part of the process. The side products generated are not detected by GC-MS and are likely to be benzene polymers. The charge required for dechlorinating all the starting material is slightly less than that required if it is a simple dechlorination reaction (*i.e.*, two electrons per chlorine). This result is in agreement with the suspected dimerizations where only one electron is required per chlorine.

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