

Electrosynthesis in systems of two immiscible liquids and a phase transfer catalyst.

V. The anodic chlorination of naphthalene

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The anodic chlorination of naphthalene in a water/methylene chloride emulsion and using tetrabutylammonium ion as the phase transfer catalyst is demonstrated; in conditions where the aqueous phase is saturated NaCl, the organic yield of 1-chloronaphthalene is 56% and the current yield is 33% after the passage of 2.33 F mol^{-1} of naphthalene. It is shown, however, that when the aqueous phase also contains zinc chloride so that the species transferred is $[(\text{C}_4\text{H}_9)_4\text{N}^+]_2\text{ZnCl}_4^{--}$, the yields can be increased to 92% and 49% respectively. The mechanism of these chlorinations is discussed.

1. Introduction

The first papers in this series discussed the effect of electrolysis parameters on the yields for cyanation [1] and acyloxylation [2] by electrolyses in water/methylene chloride emulsions when the nucleophile is fed to the anodic oxidation of an aromatic compound in the organic solvent by phase transfer catalysis from an aqueous solution. These studies had the objective of improving the yields compared to those reported in the earlier papers of Ebersson and Helgee [3-7] and, indeed, it was shown, for example, that by careful selection of the electrolysis conditions, almost quantitative yields of cyanonaphthalene could be obtained from the oxidation of naphthalene. Parts III and IV of this series [8, 9] describe a new approach to cell design for two phase electrolysis whereby a large, vertical, rotating disc electrode is half immersed in the organic phase and the other half is the aqueous solution. As the electrode rotates, electrolysis occurs in a thin film of organic solvent on the anode surface and the rest of the inter-electrode gap is filled with a highly conducting aqueous phase. Moreover the conditions are correct for rapid exchange between the phases.

This paper describes the study of the extension of the two phase electrolysis technique to chlorination, using the chlorination of naphthalene as the model reaction. In general, the chlorination of aromatic compounds might be expected to occur only with a low current efficiency because chloride is very readily oxidized and chlorine reacts rapidly with few substrates. Hence substitution required the potential to be sufficiently positive that the aromatic compound is itself oxidized and at such a potential, the oxidation of chloride ion will be mass transport controlled. As a result, the yield of chlorinated product will depend on the concentrations of both chloride ion and the organic substrate and when the substrate cation radical is otherwise stable, the highest yield of product will be achieved when the concentrations are such that the flux of chloride ion to the surface exactly balances the flux of electrophilic species away from the surface and hence no chloride will reach the electrode (this situation in homogeneous systems has already been discussed [10, 11]). In practice, the substrate cation radical may have several rapid reaction pathways available and then, for chlorination to predominate, chloride ion must be present in high concentration within

the reaction layer and chlorine evolution cannot be prevented; the optimum conditions with respect to organic yield and current efficiency may no longer be the same and each must be found by experiment.

Gourcy *et al.* [12] have recently shown that complexing the chloride ion with Lewis acids enhances substantially the yield for chlorination of aromatic hydrocarbons in one phase electrolysis. Hence we have also investigated the two phase chlorination both in the presence and absence of Lewis acids. Some experiments designed to confirm the mechanism of these two phase reactions are also discussed.

2. Experimental details

Much of the experimental procedure has been described in the earlier publications [1, 2]. The cell used for the two phase electrolysis was that described in the second paper.

In a typical two phase chlorination, 1.28 g naphthalene (0.01 mol) was dissolved in 100 cm³ CH₂Cl₂ and 3.4 g Bu₄NHSO₄ (0.01 mol) and 0.4 g NaOH (0.01 mol) were dissolved in 100 cm³ distilled water which was then saturated with NaCl. These solutions were poured into the cell, placed in an ice/water bath, and the emulsion was formed with a magnetic stirrer. After the passage of 2.33F mol⁻¹ C₁₀H₈ (2248 C) at the selected current density (e.g. 49 mA cm⁻²), the two phases were separated. The aqueous phase was washed twice with 50 cm³ of CH₂Cl₂. All portions of CH₂Cl₂ were combined and the solvent removed by evaporation at reduced pressure. The resulting oil/crystals were partitioned between ether/water and after washing and drying, the ether phase was analysed by glc using a 1.5 m OV 101 (5%) column; the column temperature was held constant at 160° C for 4 min and then programmed at 8° C min⁻¹ to 250° C. The products were identified by glc-mass spectroscopy, the chlorine isotope pattern giving firm confirmation of identity and quantitative analysis used comparison of peak areas with a standard sample of 1-chloronaphthalene.

The procedure for the electrolyses with Lewis acid present was identical except that the Bu₄NHSO₄ was not neutralized and the solutions were not neutralized after the addition of Lewis acid.

All electrolyses were carried out in duplicate and the yields from experiments under the same conditions were identical within ± 2%.

3. Results

3.1. Two phase chlorination

The electrolysis conditions for the two phase chlorinations were largely selected on the basis of experience from the earlier studies of cyanation [1] and acyloxylation [2]. Thus the electrolyses all used a water/methylene chloride emulsion where the aqueous phase was saturated with sodium chloride, a platinum anode, a naphthalene concentration in the organic phase of 0.1 mol dm⁻³ and tetrabutylammonium bisulphate as the phase transfer reagent (although (C₆H₅)₄P⁺ was shown to be an equally effective catalyst). It was thought that the current density (hence, anode potential) and the amount of Bu₄N⁺ ion in the system (which will determine the ratio of naphthalene:chloride ion concentration ratio in the methylene chloride phase) would be the parameters which most strongly effect the organic yield and current efficiency for the formation of 1-chloronaphthalene. Tables 1 and 2 show the results from the two series of electrolyses to probe the effect of variation of these parameters and it can be seen that the yields are surprisingly insensitive over a wide range of conditions. Even so the data show the advantages of a high anode current density so that the anode potential is quite positive and almost certainly at a value where naphthalene oxidation will occur and concentrations of reagents where the ratio [C₁₀H₈] : [Cl⁻] in the methylene chloride is of the order of one.

It should also be noted that both the current efficiency and organic yields for 1-chloronaphthalene are high compared with the maximum which could be obtained by one phase chlorination (see below). Indeed in acetonitrile, the maximum organic yield and current efficiency achieved were 33 and 20% even at low conversion. On the other hand, the yields from the two phase electrolysis leave room for improvement and hence the effect of complexing the chloride ion with Lewis acids was investigated. It was envisaged that the oxidation potential for the complexed chloride ion might be positive to that for naphthalene

Table 1. Effect of current density on the electrolytic chlorination of naphthalene (10 mmol) in an emulsion of CH_2Cl_2 (100 cm^3) with aqueous saturated NaCl (100 cm^3) containing Bu_4NHSO_4 (10 mmol) neutralized with NaOH . Electrolyses terminated after 2.33 F mol^{-1} of C_{10}H_8

Current density (mA cm^{-2})	% C_{10}H_8 reacted	1-chloronaphthalene		Dichloronaphthalenes
		Organic yield (%)	Current efficiency (%)	Organic yield (%)
6.5	58	43	21	3
32.5	69	45	26	7
49	70	55	33	6

oxidation permitting oxidation of the hydrocarbon without concurrent nucleophile oxidation. Moreover, Gourcy *et al.* [12] had shown the substantial improvement in yields brought about by the presence of Lewis acid in the anolyte in one phase systems.

Table 3 reports the yields of products from several two phase electrolyses where the aqueous phase contained a Lewis acid (1.5 mol dm^{-3}) + NaCl (3.0 mol dm^{-3}), i.e. a large excess of the chloroanion over the concentration of Bu_4N^+ ion. It was clear from the colouration of the organic solvent that the transition ions were, indeed, transferred and the transfer of complexed chloride could also be confirmed in experiments where transfer was permitted in the absence of naphthalene and the methylene chloride was evaporated.

It can be seen that the effect of the Lewis acids was not uniform. The presence of zinc chloride in the system leads to a substantial improvement in the yields of 1-chloronaphthalene and, indeed, with the exception of 6% dichloronaphthalenes all the naphthalene oxidized results in the formation of 1-chloronaphthalene. On the other hand, the

electrolyses in the presence of nickel, cobalt and mercuric chlorides lead to very similar organic yields of 1-chloronaphthalene as that in the absence of Lewis acid and somewhat diminished current efficiencies. The presence of tin tetrachloride and ferric chloride is certainly detrimental. It should also be noted that some Lewis acids cause a substantial increase in polychlorinated naphthalenes; particularly cobalt chloride leads to a moderate yield of a trichloronaphthalene.

The influence of zinc chloride on the selectivity of the chlorination was confirmed by carrying out a series of electrolyses to 1.0, 2.33, 3.5 and 6.0 F mol^{-1} naphthalene. The results are shown in Fig. 1. It is clear that for the first 2 F mol^{-1} that almost all the naphthalene lost is converted to 1-chloronaphthalene but thereafter the selectivity drops and dichloronaphthalene becomes an increasingly important by-product. This plot is very similar to that found earlier for the acetoxylation of 1,4-dimethoxybenzene [2].

3.2. Mechanistic studies

Several aspects of the mechanism of these chlori-

Table 2. Effect of amount of Bu_4N^+ (and hence concentration of Cl^- in the CH_2Cl_2 phase) on the electrolytic chlorination of naphthalene (10 mmol) in an emulsion of CH_2Cl_2 (100 cm^3) with aqueous saturated NaCl containing Bu_4NHSO_4 neutralized with NaOH . Electrolyses terminated after 2.33 F mol^{-1} of C_{10}H_8 . $I = 49 \text{ mA cm}^{-2}$

Bu_4N^+ (mmol)	% C_{10}H_8 reacted	1-chloronaphthalene		Dichloronaphthalenes
		Organic yield (%)	Current efficiency (%)	Organic yield (%)
1	67	46	27	2
4	75	44	28	8
10	70	56	33	6
40	65	46	26	8
100	66	35	20	8

Table 3. Electrolytic chlorination of naphthalene (10 mmol) in an emulsion of CH_2Cl_2 (100 cm^3) with water (100 cm^3) containing NaCl (0.3 mol) + MCl_n (0.15 mol) + Bu_4NHSO_4 (10 mmol) and saturated with Na_2SO_4 . $I = 49 \text{ mA cm}^{-2}$; Electrolysis to 233 F mol^{-1} of C_{10}H_8

Lewis acid	% C_{10}H_8 reacted	1-chloronaphthalene		Dichloronaphthalenes	Trichloronaphthalenes
		Organic yield (%)	Current efficiency (%)	Organic yield (%)	Organic yield (%)
None*	70	56	33	6	0
ZnCl_2	62	92	49	6	0
NiCl_2	63	52	26	11	6
CoCl_2	69	55	33	9	19
SnCl_4	54	39	18	2	4
HgCl_2	47	57	23	1	2
FeCl_3 †	70	29	17	1	0

* Solution saturated with NaCl ; no Na_2SO_4 .

† FeCl_3 (0.15 mol) + NaCl (0.15 mol).

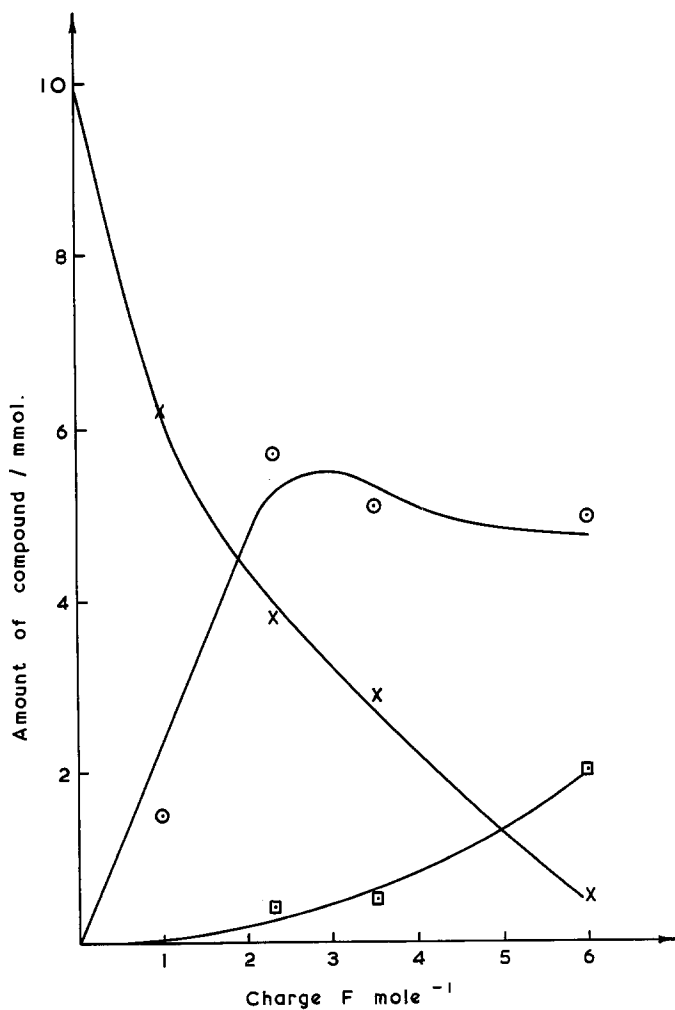


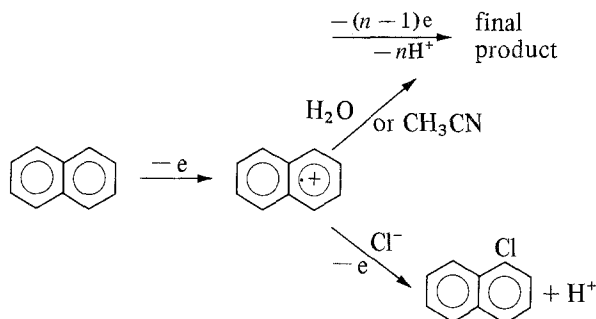
Fig. 1. Conversion of naphthalene to chlorinated products as a function of charge passed. X naphthalene, \odot 1-chloronaphthalene, \square dichloronaphthalene. Electrolysis conditions: 0.01 mol C_{10}H_8 in 100 cm^3 CH_2Cl_2 . 0.15 mol ZnCl_2 , + 0.3 mol NaCl + 0.01 mol Bu_4NHSO_4 in 100 cm^3 H_2O . $I = 49 \text{ mA cm}^{-2}$. Emulsion formed with magnetic stirrer. Temperature 5° C.

nations can be tested by cyclic voltammetry and experiments were carried out at a platinum electrode in $\text{CH}_3\text{CN}/\text{Bu}_4\text{NBF}_4$ (0.1 mol dm^{-3}) using potential scan rates in the range 0.06 to 0.6 V s^{-1} .

A cyclic voltammogram for $2 \text{ mmol dm}^{-3} \text{ Cl}^-$ in this medium shows a well formed oxidation peak with $E_{p/2} = 1.20 \text{ V}$ against an Ag reference electrode but the reduction peak on the reverse sweep, although of equal height, occurs at $E_{p/2} = 1.14 \text{ V}$; hence the Cl^-/Cl_2 couple is quasi-reversible. The cyclic voltammogram for 2 mmol dm^{-3} naphthalene shows an oxidation peak with $E_{p/2} = 1.63 \text{ V}$ but it is totally irreversible and the peak current density is unexpectedly large, almost six times that for the Cl^- solution at the same potential scan rate. This confirms that the naphthalene cation radical has no stability and that, overall, naphthalene undergoes a multi-electron oxidation.

Cyclic voltammograms were also run for solutions containing various ratios of $[\text{Cl}^-] : [\text{C}_{10}\text{H}_8]$. For solutions of $2 \text{ mmol dm}^{-3} \text{ Cl}^-$ containing 2 to 50 mmol dm^{-3} naphthalene, cyclic voltammograms run between potential limits of -0.5 V to $+1.5 \text{ V}$ showed that the peaks for $\text{Cl}^- \rightleftharpoons \text{Cl}_2$ were unaffected by the presence of naphthalene, i.e. Cl_2 does not react with the hydrocarbon. On extending the positive limit into the peak for naphthalene, the chlorine reduction peak disappears – the cation radical removes Cl^- (or Cl_2) from the reaction layer at the anode surface. In other experiments where the naphthalene concentration was held constant and the Cl^- concentration varied, the cyclic voltammograms showed the characteristics of the naphthalene oxidation peak to vary strongly with the Cl^- concentration, see Table 4. With increasing Cl^- , the oxidation peak potential shifts positive and the peak current density decreases. It is possible that the former effect is due to complexation of the hydrocarbon by Cl_2 while the latter probably

reflects a decrease in the number of electrons involved in the oxidation process, from about six in the absence of Cl^- towards two in the presence of high Cl^- concentrations. This is likely if there are several nucleophiles in the solution, i.e.



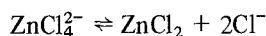
In the presence of high Cl^- concentrations a new, small peak at $E_p = 2.19 \text{ V}$ was also seen and this is likely to be the oxidation of 1-chloronaphthalene.

Controlled potential electrolyses were also carried out in acetonitrile. At $+1.5 \text{ V}$ no naphthalene was consumed while at $+2.1 \text{ V}$ a series of electrolyses terminated at $1 \text{ F mol}^{-1} \text{ C}_{10}\text{H}_8$ showed 1-chloronaphthalene to be the major product observed by glc but although the yield varied with the $[\text{Cl}^-] : [\text{C}_{10}\text{H}_8]$ ratio, the organic yield never exceeded 33%. This again suggests that other nucleophiles in solution can trap the cation radical.

The effect of ZnCl_2 on the cyclic voltammetry was also investigated. The salt $(\text{Bu}_4\text{N})_2\text{ZnCl}_4$ was first prepared and dissolved as a 2 mmol dm^{-3} solution in acetonitrile. The $I-E$ curves for this solution show the major oxidation peak to occur at 1.75 V but at all sweep rates there is a small oxidation process at $E_p \approx +1.38 \text{ V}$. Moreover this peak at $E_p = 1.38 \text{ V}$ becomes more prominent as the potential scan rate is decreased (at 0.1 V s^{-1} the ratio of peak current is 2:3, at 1.0 V s^{-1} 1:4). This suggests that although ZnCl_2 is an effective complexing agent in bulk solution, it quite readily dissociates as

Table 4. Characteristics from the oxidation peak of C_{10}H_8 in a solution of C_{10}H_8 (2 mmol dm^{-3}) in $\text{CH}_3\text{CN}/\text{Bu}_4\text{NBF}_4$ (0.1 mol dm^{-3}) containing various Cl^- concentrations

$[\text{Cl}^-]$ (mmol dm^{-3})	$E_{p/2}$ (V)	$I_{p/cv}^{1/2} A$ ($\text{A cm}^{-2} \text{ s}^{-1/2} \text{ V}^{-1/2} \text{ mol}^{-1} \text{ dm}^3$)
0	1.63	2.46
1.7	1.78	2.23
2.7	1.88	1.93
4	1.92	1.76
14	1.98	1.06



to give chloride ions and that this reaction is important in the electrochemistry of $\text{ZnCl}_2/\text{Cl}^-$ mixtures. Certainly in the situation of a steady state electrolysis, the chloride ion will be freely available. This was confirmed in experiments where solutions of both (a) aqueous saturated NaCl and (b) $1.5 \text{ mol dm}^{-3} \text{ ZnCl}_2 + 3.0 \text{ mol dm}^{-3} \text{ NaCl}$ in H_2O saturated with Na_2SO_4 , each containing $0.01 \text{ mol Bu}_4\text{NHSO}_4$ were extracted with CH_2Cl_2 ; steady state curves on the resulting CH_2Cl_2 solutions were almost identical in the potential range $+1.2$ to $+1.5 \text{ V}$.

4. Discussion

It has been shown that the chlorination of naphthalene is possible by electrolysis in $\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$ emulsions using Bu_4N^+ to transfer chloride ion from the aqueous to organic phase. Both the organic yield and current efficiency for 1-chloronaphthalene are reasonable, 56 and 33%, respectively. Furthermore, these yields are not as sensitive to current density and concentration of chloride as was expected, at least over the limited range of these parameters studied and this would certainly make the control of such electrolyses easier. The yields are certainly higher in the $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$ emulsion compared to acetonitrile but this may be due to the lower nucleophilicity of CH_2Cl_2 compared to CH_3CN . It could also imply a lower water content in the CH_2Cl_2 and that the naphthalene cation radical is so short-lived that it reacts entirely within the CH_2Cl_2 phase. Hence the major factor determining the yield of 1-chloronaphthalene may not be the number of phases. On the other hand the role of the aqueous solution in buffering the organic phase should not be underestimated. Moreover, the two phase electrolysis procedure certainly simplifies the extraction of product and allows a cleaner counter electrode reaction.

A substantial improvement in the yield of 1-chloronaphthalene is brought about by the addition of ZnCl_2 to the aqueous solution so that the species transferred between the solvents is $(\text{Bu}_4\text{N})_2\text{ZnCl}_4$. The effect of adding other Lewis acids to the aqueous chloride solution has, however, a very variable effect on the reaction. Even though the choice of Lewis acid is restricted,

because they must be stable to hydrolysis, and some of the Lewis acids studied may have particular mechanisms, e.g. with CoCl_2 the oxidation of naphthalene may occur via a Co(III) intermediate, the lack of uniformity of results between apparently similar Lewis acids casts doubts on the mechanism. Several possibilities deserve consideration:

(i) the original concept supposed that complexation of Cl^- by a Lewis acid might cause its oxidation potential to be shifted to a more positive value than naphthalene. This postulate is not supported by the $I-E$ curves obtained either for ZnCl_4^{2-} in CH_3CN or for the electrolysis system and anyway should lead to improved yields with several Lewis acids.

(ii) the Lewis acid might complex the hydrocarbon prior to oxidation or the MCl_4^- anion may act as the primary nucleophile. In the latter case the 1-chloronaphthalene would be formed by rearrangement of an intermediate, $[\text{C}_{10}\text{H}_8^+\text{MCl}_4^-]$ or $[\text{C}_{10}\text{H}_8^+[\text{MCl}_4.\text{Bu}_4\text{N}]^-]$. The success of such a route would depend on both the nucleophilicity of the MCl_4^- species and the selectivity of the decomposition of such intermediates. Such factors may not depend directly on the Lewis acidity of the metal chloride itself.

(iii) the yield of 1-chloronaphthalene may be determined only by the concentration of water in the reaction layer at the electrode surface available to trap cation radicals as unwanted products. The amount of water transferred within the hydration shell will be quite different for Cl^- , ZnCl_4^{2-} and other Lewis acid-chloride complexes.

The resolution of these mechanistic points must await further studies and it would also be interesting to investigate the chlorination of other aromatic compounds.

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