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Electrosynthesis in systems of two immiscible liquids and a phase transfer catalyst. VII. The chlorination of substituted naphthalenes

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The chlorination of 12 substituted naphthalenes by electrochemical oxidation in CH_2Cl_2/H_2O emulsions containing a phase transfer reagent, Bu_4N^+, is described. In all cases the major product can be a monochlorinated derivative, selectivity commonly 40–90%, but the efficiency and selectivity of the reactions depend on the nature and position of the substituent as well as the choice of electrolysis parameters. The anodic chlorination of naphthalenes has also been studied using cyclic voltammetry in CH_3CN and it is clear that the mechanism depends on the oxidation potential of the naphthalene.

1. Introduction

In this paper, the anodic chlorination of substituted naphthalenes in CH_2Cl_2/H_2O emulsions is discussed. The study is an extension of work on the chlorination of naphthalene reported in two earlier papers [1, 2].

The general procedure for substitution involves the electrolysis of an emulsion of a CH_2Cl_2 solution of the aromatic compound and an aqueous solution of the nucleophile (as the sodium salt) and a phase transfer reagent, e.g. Bu_4N^+. The reactions are considered to occur at the anode–organic solvent interface via cation radical intermediates and the role of the phase transfer reagent is to supply the nucleophile to the organic medium. Such procedures have the advantages of good yields at reasonable current densities using very simple cells, and the work-up of the product is also very straightforward. This type of electrolysis is generally considered to date from 1974 and a paper by Eberson and Helgee [3], although it is interesting to note a 1958 thesis [4] which describes the chlorination of naphthalene under apparently similar conditions. In the last 10 years, two-phase electrolysis has been used for cyanation [5–9] and acyloxylation [10–14] of several molecules as well as chlorination. Feess and Wendt [15] have reviewed the literature on two-phase electrolysis.

It remains difficult to design experiments which probe critically the mechanism of reactions in emulsions. It is therefore convenient to assume that the anode reaction occurs in the organic phase and hence that cyclic voltammetry carried out in an aprotic solvent leads to information relevant to the emulsion system. We have used acetonitrile (a slightly better solvent for electrochemistry than CH_2Cl_2) as a medium for our mechanistic studies. The mechanisms of anodic halogenation have been reviewed [16, 17] and in the case of chlorination, mechanisms involving cation radicals are regarded as unusual because of the low potential for chloride oxidation. Reactions involving molecular or atomic chlorine are believed to be more common, although in a few cases it has been demonstrated that substitution only occurs at potentials where the organic substrate is oxidized. Substitution is then dependent on 'flux balancing'. By control of the bulk concentrations of chloride

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and the organic molecule and hence their fluxes to the anode surface, it is possible to arrange conditions so that all incoming chloride ions react with cation radicals before being oxidized at the anode [18, 19]. The last few years have seen a recognition that the reactions of cation radicals with nucleophiles need not be simple, and the complications which arise have been reviewed by Parker [20, 21].

2. Experimental details

All reagents were obtained from commercial sources and for preparative electrolyses were used as supplied. Electrolyses were performed at constant current using a modified Chemical Electronics Potentiostat. The closed beaker type cells and the product extraction procedures have been described elsewhere [2].

Experiments in which the reaction progress was monitored as a function of charge were analysed on a Varian 3700 chromatograph by direct injection of the CH_2Cl phase on to a 1.3 m, 5% OV101 column, typically run isothermally at about 200° C. A Perkin–Elmer 8310 chromatograph fitted with a 12 m dimethyl siloxane capillary column was also used to provide more accurate information on isomer distributions. The products obtained on electrolysis of each naphthalene derivative were characterized by comparison of retention times with authentic samples, when available, and by GLC–mass spectroscopy. The major monochlorinated product from 1-fluoro-naphthalene was isolated by elution through an activated basic aluminium oxide chromatography column with hexane and by HPLC with 90% aqueous MeOH on a ZORBAX ODS (9.4 mm × 25 cm) column. The white needle-shaped crystals were analysed by 360 MHz, ^1H and ^{13}C NMR.

Cyclic voltammetry was carried out on 5 mM solutions of naphthalene in acetonitrile (distilled from $KMnO_4$ and CaH_2) and 0.1 M tetrabutylammonium tetrafluoroborate. A three-electrode, two-compartment cell was used with a 0.2 cm^2 platinum disc working electrode and platinum wire loop counter electrode. A silver wire immersed in 0.1 M $AgNO_2$ served as a reference electrode and was separated from the working electrode by a Luggin capillary and glass frit. The potentiostat was a Hi-Tek DT2101 and was driven by a Hi-Tek PPR1 waveform generator. The working electrode was polished before every sweep on 0.05 μm alumina.

3. Results

3.1. *Preparative electrolyses*

Preparative scale electrolyses were carried out on 13 naphthalenes under conditions selected on the basis of earlier experience with the parent compound [1, 2]. The results of these experiments, together with the peak potentials for the oxidation of the naphthalenes determined by cyclic voltammetry at 0.1 V s^{-1} in acetonitrile, are reported in Table 1. A number of features should be noted.

(i) There appears to be an approximately linear correlation between the oxidation potential and the rate of oxidation of the naphthalene, indicated in the table by the percentage of unreacted naphthalene after a charge equivalent to 2*e* per molecule. With the naphthalenes most readily oxidized, the substrate consumption is about 70%, but the most deactivated naphthalenes are only consumed to an extent of about 25%. On the other hand there is no correlation between oxidation potential and selectivity. Such data suggest that a competitive anode reaction, e.g. water oxidation or oxidation of Cl^- in the aqueous phase, becomes more important with the deactivated naphthalenes, but the change in the importance of the competing reaction is minor considering the large change in oxidation potentials of the naphthalenes.

(ii) The major product is usually a monochlorinated derivative of the starting material and commonly the selectivity for this conversion is good, in the range 40–90%. In fact, in most cases,

Table 1. Chlorination of naphthalenes in CH_2Cl_2/H_2O emulsions; 10 mmol naphthalene in 100 cm^3 CH_2Cl_2 + 100 mmol NaCl + 10 mmol Bu_4NHSO_4 + 10 g Na_2SO_4 in 100 cm^3 H_2O; I = 50 mA cm^{-2}; undivided cell

Naphthalene	E_p/V *vs Ag/Ag*$^+$	*Unreacted naphthalene*[a] *(%)*	*Monochlorinated products*[a] *(%)*	*Selectivity*[b] *(%)*	*Isomer ratio*[c]
1-OC_2H_5	0.97	32	33	48	24:64:12
1-OCH_3	1.02	21	16	20	24:76
2-OCH_3	1.06	36	52	81	5:95
1-Me	1.28	43	10	18	21:30:49
2-Me	1.29	38	31	50	90:10
Unsubstituted	1.36	30	39	56	100
1-Br	1.38	39	28	46	100
1-Cl	1.39	45	41	75	1:95:4
1-F	1.47	56	41	94	87:4:9
1-$COOCH_3$	1.47	54	46	99	10:3:87
1-$COCH_3$	1.62	61	23	59	2:16:82
1-NO_2	1.82	75	20	82	6:6:88
1-CN	1.85	75	19	77	14:78:7

[a] Electrolysis terminated after 2*e* per molecule.
[b] To monochlorinated products.
[c] Monochlorinated products.

several isomers are formed as substitution occurs at several ring positions. However, one isomer usually predominates strongly; the table reports the isomer distribution in the order of elution from the GLC.

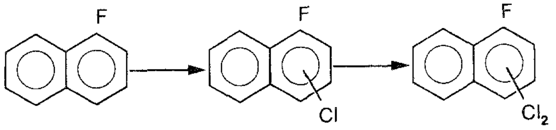
(iii) Where the selectivity is poor there is usually a clear reason. Either (a) the reaction does not proceed via nucleophilic attack of Cl^- on the cation radical (see later), or (b) the cation radical has alternative chemistry, e.g. with 1-methylnaphthalene substitution occurs in the side chain and even the major monochlorinated product is the –CH_2Cl derivative.

(iv) Dichlorinated products are usually observed as minor products after 2*e* per molecule, but on continuation of the electrolyses these become more important.

(v) With 1-bromonaphthalene, a second product is formed in a similar yield to that of the chlorobromonaphthalene. This second product is 1-chloronaphthalene, and such a displacement product was not observed with any other substituted naphthalene.

(vi) The products from the oxidation of 1-fluoronaphthalene were separated by HPLC and the major isomer of the chlorinated product was examined by 360 MHz NMR. The splitting pattern for the ring protons show the major product to be 4-chlorofluoronaphthalene.

With several of the substituted naphthalenes the distribution of products was monitored as a function of charge passed. Fig. 1 shows two typical plots. Fig. 1a shows data for 1-fluoronaphthalene. It can be seen that initially the substrate is consumed relatively rapidly and chlorofluoronaphthalene is the major product. As the electrolysis is continued, the rate of consumption of 1-fluoronaphthalene decreases, the amount of monochlorinated products in solution passes through a peak and the dichlorofluoronaphthalenes increase steadily. This is the form of data to be expected for a controlled current electrolysis when the substitution is sequential, i.e.



particularly when the chlorination step does not lead to a large change in oxidation potential. In fact this change in oxidation potential is small; the values for naphthalene and 1-chloronaphthalene

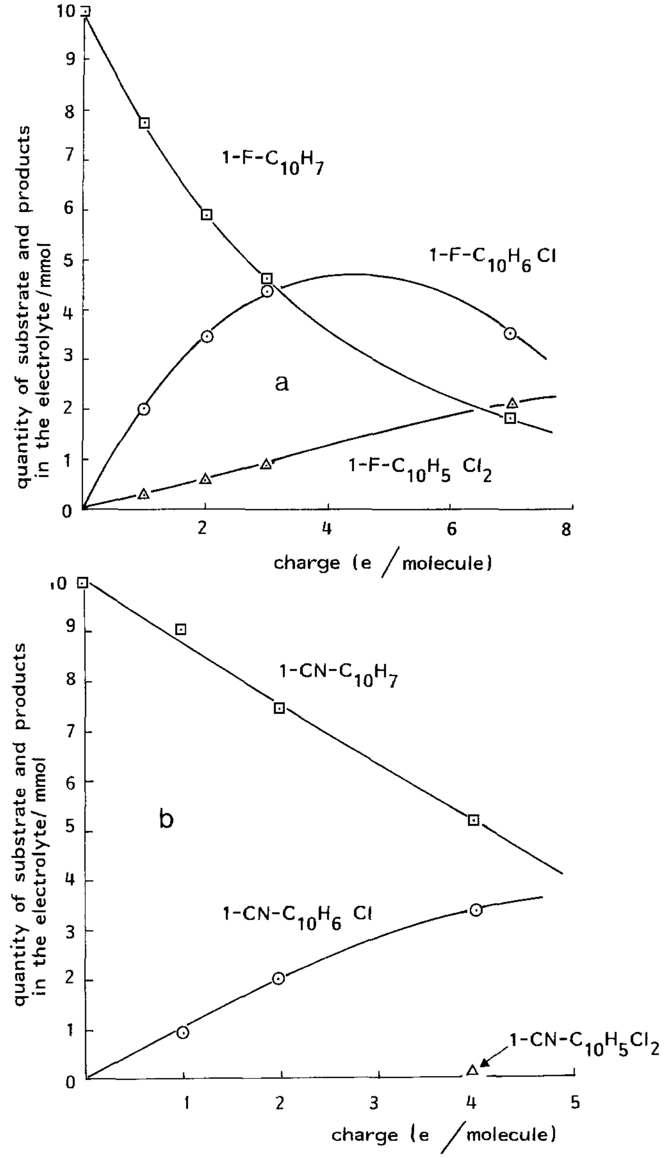


Fig. 1. Distribution of products as a function of charge passed for electrolyses of (a) 1-fluoronaphthalene, (b) 1-cyanonaphthalene. Conditions as in Table 1.

differ by only 30 mV. Fig. 1b shows the data for 1-cyanonaphthalene and the same trends are present, although the low rate of substrate consumption displaces the maximum in the chlorocyanonaphthalene curve and the formation of dichloro products to much higher charge consumption. Similar sequential chlorination steps were found with naphthalene [1, 2].

The conditions used to obtain the data in Table 1 should not necessarily be regarded as the best with respect to conversion or to selectivity to monochlorinated products. Indeed, it was shown above that both the yield and selectivity to monochlorinated products are a function of charge passed. Hence a number of electrolysis parameters were investigated. However, it was found that, in general, the products from electrolyses were surprisingly insensitive to temperature, current density and the ratio of the solvents in the emulsion. Thus, for example, with naphthyl acetate, the yield and selectivity to the monochlorinated product were similar when the ratio of CH_2Cl_2 to water was 1 : 1 and 1 : 9. Adding $ZnCl_2$ to the aqueous medium [1, 2] does influence the electrolyses but not always to advantage and these effects are discussed in the following section.

Table 2. Comparison of electrolysis with chemical reaction of 1-methoxynaphthalene with Cl_2 in the emulsion

	1-methoxynaphthalene consumed (%)	*Selectivity (%)*[a]	*Isomer distribution*
Electrolysis[b]	70	49	19:81
Chemical reaction[c]	29	70	16:84

[a] Monochlorinated products.

[b] 1 mmol 1-methoxynaphthalene; $I = 25\,\mathrm{mA\,cm^{-2}}$; other conditions as Table 1.

[c] 1 : 10 mixture of $Cl_2 : N_2$ for 90 min; 5 mmol 1-methoxynaphthalene.

In a series of electrolyses with 1-methoxynaphthalene, where the concentration of substrate was decreased (10, 5 and 1 mmol in $100\,\mathrm{cm^3}$ CH_2Cl_2) but the current density was maintained constant at $50\,\mathrm{mA\,cm^{-2}}$, very unexpected results were obtained. The current efficiency, selectivity and isomer distribution of monochlorinated products were the same even though, with the lowest concentration, the estimated limiting current density was below the current density used. As a result it was necessary to consider the possibility that the products were arising from the reaction of molecular chlorine with the neutral naphthalene in bulk solution. To test this hypothesis a 1 : 10 mixture of Cl_2 in N_2 was passed through the emulsion with a flow rate of $20\,\mathrm{cm^3\,min^{-1}}$ for 90 min (in total, an amount of Cl_2 in slight excess of 2*e* per molecule of 1-methoxynaphthalene). The results of this experiment are compared with an electrolysis in Table 2 and it can be seen that there are very strong similarities in the data.

3.2. *Influence of zinc chloride*

It was found in earlier studies [1, 2] that the addition of $ZnCl_2$ to the aqueous medium, so that the anion transferred was $ZnCl_4^{2-}$, led to a significant improvement in the selectivity for the conversion of naphthalene to 1-chloronaphthalene. It was therefore considered worthwhile to examine the effect of adding $ZnCl_2$ to the emulsion oxidation of substituted naphthalenes. In addition, a few further experiments have been carried out to probe the origin of the effect.

Table 3 compares data for six naphthalenes with and without $ZnCl_2$. The improvement in the selectivity of naphthalene to 1-chloronaphthalene conversion is again confirmed, although it should be noted that this improvement is achieved by a reduction in the consumption of naphthalene rather than an increase in rate of production of 1-chloronaphthalene. With all five substituted naphthalenes there is also a decreased consumption of the starting material in the presence of $ZnCl_2$, but no corresponding increase in selectivity. Indeed with three of the naphthalanes, side reactions clearly become more important. The isomer distribution is generally similar with and without $ZnCl_2$, the

Table 3. Influence of $ZnCl_2$ (50 mmol) on the emulsion electrolyses of naphthalenes. Conditions as Table 1.

Naphthalene	*Without $ZnCl_2$*			*With $ZnCl_2$*		
	Unreacted naphthalene (%)	*Selectivity to monochlorinated products (%)*	*Ratio of isomers*	*Unreacted naphthalene (%)*	*Selectivity to monochlorinated products (%)*	*Ratio of isomers*
Unsubstituted	40	59	100	59	80	1:95:4
1-Chloro	45	75	1:95:4	57	73	1:95:4
1-Fluoro	48	84	89:5:6	54	40	97:1:2
1-Methoxy	29	31	24:76	49	13	10:90
1-Ethoxy	32	48	24:64:12	50	18	27:65:8
1-Methyl	43	23	21:30:49	48	32	15:76:9

exception being 1-methylnaphthalene where the addition of $ZnCl_2$ leads to a steep decrease in side chain substitution.

It was reported previously [2], and confirmed in this study, that the consumption of naphthalene in the presence of $ZnCl_2$ is much higher in a divided than an undivided cell, although the selectivity to 1-chloronaphthalene is very high in both types of cell. This, combined with the observation that in the undivided cell the consumption of naphthalene is much reduced and less dichloro products are formed in the presence of $ZnCl_2$, prompts the postulate that the back reaction, the cleavage of C–Cl bonds, may occur at the cathode and then be enhanced by the presence of zinc metal. Several experiments were attempted to test this idea.

(i) Chlorinations of naphthalene were carried out without $ZnCl_2$ in solution using the normal nickel gauze cathode and a zinc electroplated, nickel gauze cathode. The consumption of naphthalene was markedly decreased with the zinc cathode (60 to 43%) and the selectivity increased a little (56 to 65%).

(ii) During the chlorination of 1-chloronaphthalene the solution was monitored for the presence of naphthalene. Both with and without $ZnCl_2$, none was found.

(iii) Using a divided cell the reduction of 1-chloronaphthalene was investigated. Using the normal emulsion conditions it was clear that gas evolution, i.e. hydrogen, was always a major cathode process. In the presence of $ZnCl_2$ zinc deposition also occurred, but the yield of naphthalene was 0 in the presence of $ZnCl_2$ and $< 5\%$ in its absence.

Overall it is clear that the reductive cleavage of C–Cl bonds at the cathode is never important.

Another factor considered, but ruled out, was the pH of the electrolyte. In an undivided cell and without $ZnCl_2$ two factors influence the electrolyte pH: (i) the substitution reaction at the anode leads to $1H^+$ per $2e$, and (ii) H_2 evolution at the cathode leads to $2OH^-$ per $2e$, and the electrolyte may become less acid with time. Adding $ZnCl_2$ will cause a major change in the cathode reaction to zinc deposition and hence the electrolyte will probably become acidic; certainly in a divided cell the anolyte will become acid. However, the addition of $ZnCl_2$ and the introduction of a cell divider have opposite effects on the rate of consumption of the naphthalene.

Hence we believe that the influence of $ZnCl_2$ arises from two factors.

(i) In an undivided cell the consumption of all naphthalenes is reduced by $ZnCl_2$ in solution. We suggest that some hydrocarbon reduction occurs at nickel, perhaps via adsorbed hydrogen atoms species, but not at zinc. Clearly a cell divider also prevents the reduction of the naphthalene.

(ii) The Zn(II) influences the chemistry of intermediates formed at the anode, maybe by the formation of σ complexes between $ZnCl_4^{2-}$ and the hydrocarbons [22]. In the case of naphthalene these changes are favourable and a possible effect is a reduction in the amount of polymerization. With the substituted naphthalenes, the changes in chemistry are detrimental.

3.3. *Mechanistic studies*

Cyclic voltammograms were recorded for each of the naphthalenes ($\sim 5\,\mathrm{mmol\,dm^{-3}}$) in CH_3CN/ Bu_4NBF_4 ($0.1\,\mathrm{mol\,dm^{-3}}$) at a platinum electrode. Potential scan rates over the range 25–200 $\mathrm{mV\,s^{-1}}$ were used. Each gave well-formed but totally irreversible oxidation peaks. The peak potentials at $0.1\,\mathrm{V\,s^{-1}}$ are reported in Table 1 and plots of the current function ($I_p/C\ v^{1/2}$, where I_p is the peak current density, C the concentration of naphthalene and v the potential scan rate) versus potential scan rate for some typical naphthalenes are shown in Fig. 2. The current function is proportional to the number of electrons involved in the oxidation of the naphthalene. Hence by comparison of the current functions with that of ferrocene (which is oxidized in a reversible $1e$ process) it can be seen that in acetonitrile without added nucleophiles, the oxidation of the naphthalenes are 2 to $4e$ per molecule processes on this timescale.

Cyclic voltammograms were also run for the naphthalenes in the presence and absence of excess chloride ion. Two types of responses were obtained and typical sets of such voltammograms are

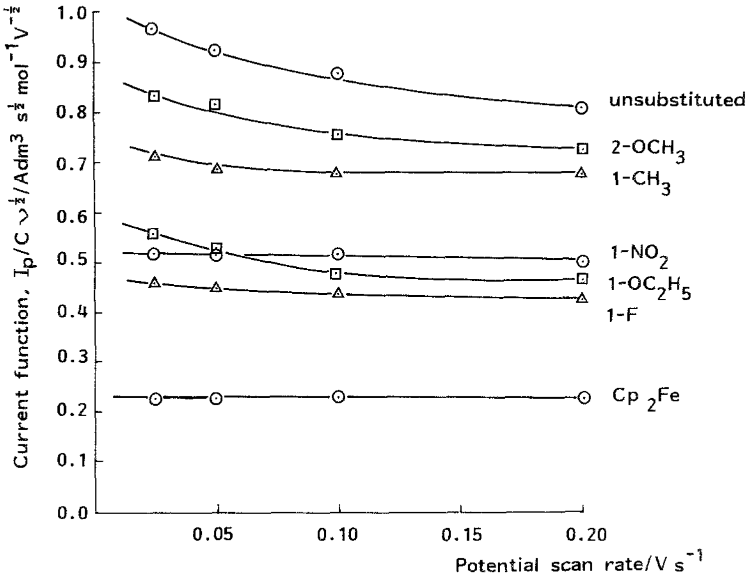


Fig. 2. Current functions versus potential scan rate plots for a series of naphthalenes. Platinum electrode in CH_3CN/Bu_4NBF_4 (0.1 mol dm^{-3}).

shown in Figs 3 and 4. The behaviour shown in Fig. 3 was found for the three alkoxynaphthalenes investigated, while that in Fig. 4 is the response with all other naphthalenes.

In the absence of a naphthalene, the Cl^-/Cl_2 couple gives an anodic peak at +0.73 V and a coupled cathodic peak at +0.45 V. Curve a in Fig. 3 is the voltammogram for 1-ethoxynaphthalene and curves b and c the cyclic voltammograms for the mixture of 1-ethoxynaphthalene and chloride ion with different positive limits. It can be seen that there is no chlorine reduction peak and only a small peak for the oxidation of the naphthalene. These features are a clear indication that the Cl_2 reacts with 1-ethoxynaphthalene even on the timescale of cyclic voltammetry. This is consistent with the results of passing Cl_2 gas through solutions of the naphthalene.

Fig. 4 shows data from the same series of experiments with 1-fluoronaphthalene and the results are quite different. In the voltammograms of the Cl^-/hydrocarbon mixture and with both positive limits, the Cl_2 reduction peak is clearly observed (although slightly shifted when the positive limit is + 1.7 V). Moreover, the naphthalene oxidation peak is still very prominent in the presence of Cl^-.

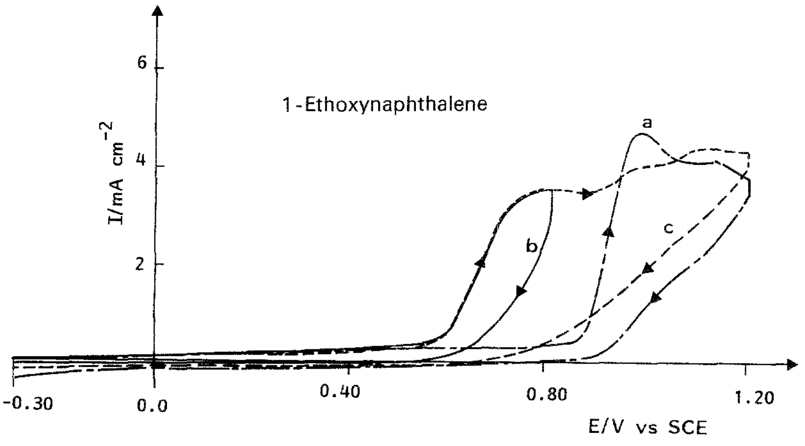


Fig. 3. Cyclic voltammograms for: (a) 5.17 mmol dm^{-3} 1-ethoxynaphthalene; (b, c) 5.17 mmol dm^{-3} 1-ethoxynaphthalene + 20 mmol dm^{-3} Et_4NCl. The positive limit is 0.80 V in (b) and 1.2 V in (c). Platinum electrode in CH_3CN/Bu_4NBF_4. Potential scan rate, 0.1 V s^{-1}.

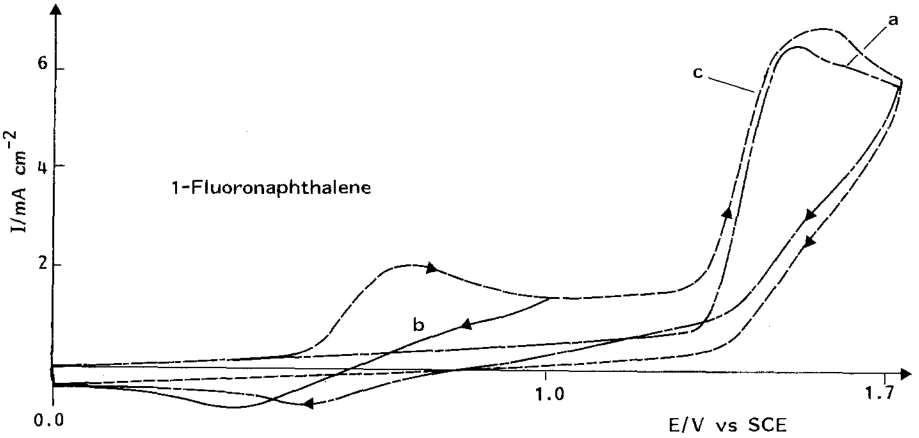


Fig. 4. Cyclic voltammograms for: (a) 4.94 mmol dm^{-3} 1-fluoronaphthalene; (b, c) 4.94 mmol dm^{-3} 1-fluoronaphthalene + 20 mmol dm^{-3} Et_4NCl. The positive limit is 0.85 V in (b) and 1.7 V in (c). Platinum electrode in CH_3CN/Bu_4NBF_4. Potential scan rate 0.1 V s^{-1}.

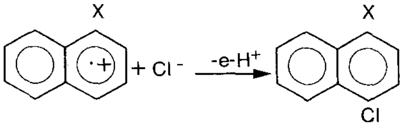
4. Discussion

The results show the chlorination of substituted naphthalenes to be a general reaction although the current efficiencies and the selectivity depend on the nature and position of the substituent.

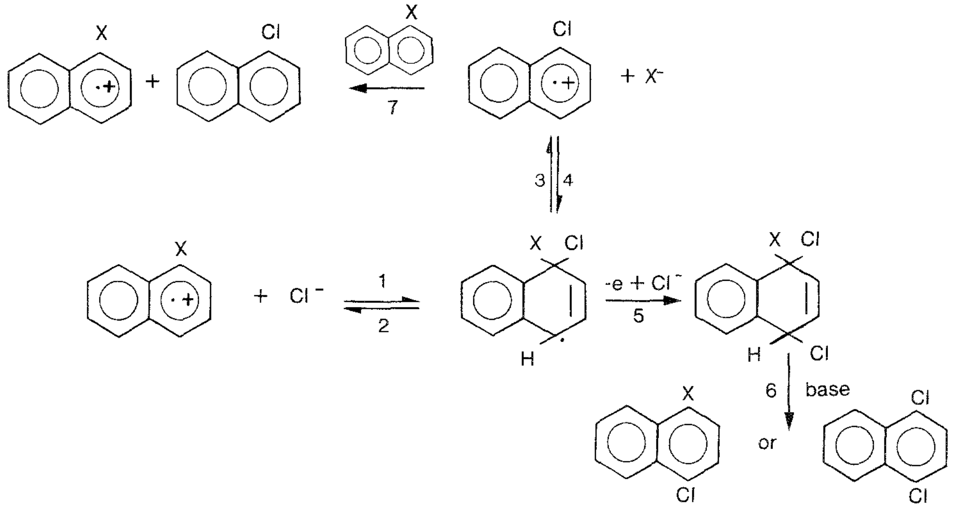
The current efficiencies for the oxidation of the naphthalenes correlate with their oxidation potentials. Between 25 and 80% of the charge is used in the monochlorination of the naphthalenes and, since there is no evidence that the extent of polychlorination varies, it appears that a parallel electrode reaction occurs. This is most likely to be oxygen or chlorine evolution. The importance of this reaction does not, however, vary strongly with potential (NB the oxidation potentials of the substituted naphthalenes vary over the range 0.97–1.85 V) and the extent of this reaction may depend on a secondary factor, e.g. the wetting of the platinum anode surface by the aqueous and organic phases.

The selectivity of the reactions depends on several factors. Most importantly, it depends on the type of mechanism involved. There is strong evidence, from both cyclic voltammetry and preparative scale experiments, that those naphthalenes readily oxidized (i.e. the alkoxynaphthalenes), are substituted via a mechanism involving Cl_2. Even though the first step may be an electron transfer to give the cation radical and chloride ion, the cation radical is formed in a different environment away from the electrode surface. With the other naphthalenes we believe that an essential first step is their oxidation to cation radicals at the electrode surface. In constant current electrolyses this can be the major reaction since the cation radicals react with Cl^-, thus preventing the chloride ion reaching the surface and being oxidized to Cl_2 [18, 19].

The selectivity also depends strongly on the chemistry of the cation radicals. This chemistry is known to vary markedly with subtle changes in the structure of the cation radical [20, 21]. A factor which influences the chemistry is the electron distribution in the cation radical, both the position and intensity of the charge being important. Unfortunately, few calculations have been published for substituted naphthalenes [17, 23, 24]. It appears, however, that for cation radicals with electron donating groups in the 1-position, the most intense positive charge occurs at the 4-position, so that the expected reaction with nucleophiles is



On the other hand, strongly electron-withdrawing substituents give cation radicals where the charge is mainly centred at the 1-position. The mechanism



explains many of the observed product distributions. The oxidation of 1-fluoronaphthalene led to 1-fluoro-4-chloronaphthalene by the sequence of reactions 1, 5 then 6. The importance of the displacement reaction depends on the relative rates of 2, 3 and 5. The competition between loss of Cl^- and X^-, steps 2 and 3, is largely determined by the relative leaving group abilities. Probably only in the case of Br^- is loss of X^- rather than Cl^- expected and with 1-bromonaphthalene, 1-chloronaphthalene was a major product.

The addition of $ZnCl_2$ was found to be significantly advantageous only with the unsubstituted naphthalene. While $ZnCl_2$ always modifies the product distribution after 2*e* per molecule, the yield of monochlorinated products is not generally improved.

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