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Electrosynthesis in systems of two immiscible liquids and a phase transfer catalyst. VI. The influence of zinc chloride on the chlorination of naphthalene

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The influence of zinc chloride on the chlorination of naphthalene by electrolysis in a water–methylene chloride emulsion and using tetrabutylammonium ion as a phase transfer catalyst is described. It is shown that when the aqueous medium contains both NaCl and $ZnCl_2$ it is the anion $ZnCl_4^{2-}$ which transfers into the organic phase and it is confirmed that the presence of $ZnCl_2$ in the electrolyte is, indeed, beneficial. The electrolyses have been carried out in both divided and undivided cells and in both the organic yield of 1-chloronaphthalene can exceed 80% but the former is better from the viewpoint of speed of electrolysis; in the divided cell, the conversion was 85% (cf. typically 60% in the undivided cell) after the passage of 2.3 F mol^{-1} of naphthalene. Possible mechanisms for the effect of $ZnCl_2$ are discussed.

1. Introduction

In the previous paper of this series [1] it was shown that the technique of nucleophilic substitution by electrolysis in methylene chloride–water emulsions containing a phase transfer agent could be extended to chlorination. It was reported that the chlorination of naphthalene led to 1-chloronaphthalene with an organic yield of about 55%. In addition, it was noted that the addition of $ZnCl_2$ to the electrolyte led to a substantial increase of the organic yield; it was supposed that in this system it was the anion, $ZnCl_4^{2-}$ which was transferred to the organic medium although it was also found that several other metal ions, each capable of forming similar anionic chlorocomplexes and apparently transferred to the methylene chloride phase, did not lead to a similar increase in yield of 1-chloronaphthalene. Hence it was the purpose of the work reported here to investigate in more detail the role of the zinc species in the reaction.

A number of mechanisms have been considered to explain the enhancement of the yield of 1-chloronaphthalene.

(a) An early concept was that in the $ZnCl_4^{2-}$ solution the chloride would be complexed, perhaps to an extent that naphthalene would become the most readily oxidized species in the system. *I–E* curves previously reported [1] showed that this was not the case and that the shift in the oxidation potential of chloride ion is only small because of the equilibrium

$$[(Bu_4N^+)_2\ ZnCl_4^{2-}] \rightleftarrows [Bu_4N^+\ ZnCl_3^-] + [Bu_4N^+Cl^-] \qquad (1)$$

(b) It was felt that the nucleophilic properties of $ZnCl_4^{2-}$ and Cl^-, although in the form of ion aggregates, might be quite different.

(c) The zinc species could be involved in the formation of π-complexes with naphthalene or reaction products or the stabilization of intermediates.

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(d) The extent of hydration of $ZnCl_4^{2-}$ and Cl^- in the organic phase will also be different. While the methylene chloride is, of course, saturated with water, there might still be differences in the quantities of water intimately available at the site of reaction between the cation radical and nucleophile. Certainly the reaction of water with the cation radical will lead to unwanted products such as naphthol or naphthaquinone.

(e) All the earlier work used undivided cells. Hence it was possible that zinc metal could be formed at the cathode and be involved in the dechlorination of polychloroderivatives formed at the anode back to naphthalene or 1-chloronaphthalene.

2. Experimental details

Electrolyses were carried out with a constant current at room temperature and the emulsion of the methylene chloride and the aqueous solution was always formed with a rapidly rotating magnetic stirrer within the cell (if visible droplets are present in the electrolyte, the yield of products are substantially diminished). Experiments were performed in both undivided and divided cells. The former was an enclosed beaker, volume 400 cm^3, containing a 15 cm^2 platinum gauze anode and nickel gauze cathode and fitted with a water cooled condenser. The cell was filled with 100 cm^3 methylene chloride and 100 cm^3 of aqueous solution. The divided cell was a simple H-cell with two Pt gauze electrodes separated by a fine glass frit and the anolyte compartment was fitted with a condenser. The anolyte was an emulsion of 75 cm^3 methylene chloride and 75 cm^3 of aqueous phase while the cathode compartment was 35 cm^3 of aqueous $ZnCl_2$ + NaCl. The exact solution composition and other conditions are shown in each table and figure.

The constant current source was a modified Chemical Electronics transistorized potentiostat 70V/2A and charges were measured using a laboratory built digital coulometer. Glc analyses of solutions during and after electrolyses were carried out with a Varian chromatograph with data analysis system. An OV 101 column (2 m) was used; a temperature programme with 4 min at 160° C followed by an increase to 300° C at 8° C min^{-1} was found to give the best separation. The N_2 carrier gas flow rate was 20 cm^3 min^{-1}.

At the end of the electrolysis a known amount of an internal standard, 1-bromonaphthalene, in ether was added to the emulsion electrolyte and the two phases were allowed to stand for 30 min. The aqueous phase was extracted with several portions of methylene chloride. The methylene chloride fractions were then combined and the solvent removed on a rotary evaporator. The residue was partitioned between ether and water (to remove Bu_4N^+ salts) and the ether phase was dried with $MgSO_4$ and made up to a known volume for glc analysis.

Where analyses were carried out repetitively during electrolyses, either 5 cm^3 samples of the methylene chloride phase was treated in a similar

Table 1. Partition data for Zn(II), Cl^- and H_2O for the water–methylene chloride system containing Bu_4N^+

*Initial materials (mmol)**			*At equilibrium (mmol)†*			
NaCl	*$ZnCl_2$*	*Bu_4NHSO_4*	*Aqueous phase Zn(II)*	*CH_2Cl_2 phase*		
				Zn(II)	*Cl^-*	*H_2O*
50	1	5	0.1	0.8	5.7	–
50	5	5	2.8	2.1	9.6	8.8
50	25	5	21.7	2.4	9.8	–
50	5	0	–	0.1	0.1	–
50	5	2.5	3.5	1.6	4.6	–
50	0	5	–	–	2.5	10.6
0	0	0	–	–	–	5.1

* always in 50 cm^3 H_2O + 50 cm^3 CH_2Cl_2

† Zn(II) by atomic absorption spectroscopy, Cl^- by gravimetric analysis (as AgCl), H_2O by automated Karl Fischer titration.

way to above or a sample of the methylene chloride phase was injected directly onto the glc column.

3. Phase transfer equilibria

Table 1 reports the data from a series of experiments designed to define the partition of zinc(II) and chloride ion between water and methylene chloride in the presence of tetrabutylammonium ion as the phase transfer catalyst, and the extent to which water dissolves in methylene chloride in the presence of the various components of the system.

It is clear that Zn(II) only transfers to the organic phase in the presence of Bu_4N^+. When there is a deficiency of the phase transfer reagent, the ratio of Zn(II) in CH_2Cl_2 to the total Bu_4N^+ approaches 1:2 while the ratio of Zn(II) to Cl^- in methylene chloride is approximately 1:4.5. These ratios are compatible with an equilibrium involving the ion aggregate $[(Bu_4N^+)_2ZnCl_4^{2-}]$, more than 80% of this species being in the organic phase. The excess Bu_4N^+ takes part in a partition equilibrium involving chloride ion. The data for water is also interesting; as expected, ions in the system increase the solubility of water in methylene chloride but the transfer of $ZnCl_4^{2-}$ takes with it less water than Cl^-. The difference in the hydration of $ZnCl_4^{2-}$ and Cl^- could be significant when the hydration of Bu_4N^+ is taken into account even if this cation is only poorly hydrated.

4. The effect of electrolysis parameters on the yield of 1-chloronaphthalene

Several series of oxidations of naphthalene were carried out in the methylene chloride–aqueous sodium chloride emulsions containing tetrabutylammonium ion as a phase transfer catalyst. Amongst the parameters varied were the concentrations of zinc chloride, naphthalene and tetrabutylammonium ion, current density, anode material and conversion and the electrolyses were also carried out in both divided and undivided cells; the results are summarized in Tables 2 to 6.

Table 2 reports data from a series of experiments where the concentration of zinc chloride in the aqueous phase was varied while the total chloride ion concentration was maintained constant. Firstly it can be seen that these data confirm the earlier observation [1] that the addition of zinc chloride to the system increases the selectivity for 1-chloronaphthalene (throughout the paper, selectivity is defined as the % organic yield of product based on the naphthalene consumed). Moreover most of the increase in selectivity could be achieved by a relatively small addition of zinc chloride. It should be noted, however, that the change in selectivity, in fact, largely arises from a decrease in the consumption of naphthalene rather than an increase in the amount of 1-chloronaphthalene formed, i.e. the current yield of 1-chloronaphthalene is unchanged. On the other

Table 2. Effect of the concentrations of $ZnCl_2$ and NaCl in the aqueous phase on the chlorination of naphthalene. Electrolysis conditions: 10 mmol $C_{10}H_8$ in 100 cm^3 CH_2Cl_2 + 10 mmol Bu_4NHSO_4, NaCl, $ZnCl_2$ and 9 g Na_2SO_4 in 100 cm^3 H_2O. Undivided cell with Pt anode and Ni cathode. $I = 50\ mA\ cm^{-2}$. Electrolyses terminated after 2.33 F mol^{-1} of $C_{10}H_8$

Electrolytes (mmol)		*$C_{10}H_8$ consumed (%)*	*$C_{10}H_7Cl$ produced (mmol)*	*Selectivities (%)*	
$ZnCl_2$	*NaCl*			*$C_{10}H_7Cl$*	*$C_{10}H_6Cl_2$*
0	600	73	4.3	59	10*
25	550	65	4.7	72	7
50	500	63	4.5	71	6
100	400	63	4.5	71	6
150	300	60	4.6	77	5

* In this electrolysis, about 3% $C_{10}H_5Cl_3$ was also observed.

Table 3. Effect of naphthalene concentration and charge passed on the two phase chlorination reaction. Electrolysis conditions: $C_{10}H_8$ in 100 cm^3 CH_2Cl_2 + 0.15 mol $ZnCl_2$, 0.3 mol NaCl, 9 g Na_2SO_4 and 10 mmol Bu_4NHSO_4 in 100 cm^3 H_2O. Undivided cell with Pt anode and Ni cathode. $I = 50$ mA cm^{-2}.

Initial $C_{10}H_8$ (mmol)	Q(F mol^{-1})	$C_{10}H_8$ consumed (%)	Selectivity $C_{10}H_7Cl$ (%)
10	1.0	44	59
	2.33	64	74
100	1.0	36	53
	2.0	50	77
	2.33	55	83

hand the presence of zinc chloride also apparently diminishes the formation of di- and poly-chlorinated naphthalene during the first 2.33 F mol^{-1} of electrolysis.

Table 3 demonstrates that the concentration of naphthalene could be increased without loss in selectivity; the actual concentrations of naphthalene in the organic phase are 0.1 and 1.0 mol dm^{-3}. This table also shows an interesting feature of the data found repeatedly during the study. That is, the selectivity of 1-chloronaphthalene after the passage of 1 F mol^{-1} is low but that it recovers by the time the electrolysis has been continued to 2.33 F mol^{-1}. A corresponding feature is not seen in the consumption of naphthalene and this raises the possibility that there is an intermediate in the conversion of naphthalene to 1-chloronaphthalene present as a stable species in the electrolyte at the early stage of the electrolysis. This possibility will be discussed later.

Table 4 shows the effect of current density on the electrolysis. In the chlorination of naphthalene, a high selectivity for 1-chloronaphthalene requires the oxidation at the electrode surface of the aromatic hydrocarbon despite the fact that its oxidation potential is more positive than that of the nucleophile. Also both a high selectivity and a high current yield are dependent on balancing the flux of cation radical away from the anode surface with the flux of nucleophile to the surface; the flux of $ZnCl_4^{2-}$ or its ion aggregate to the surface is essentially controlled by the bulk concentration of $(Bu_4N^+)_2ZnCl_4^{2-}$ in the methylene chloride phase and therefore, in our conditions, the concentration of tetrabutylammonium ion. In an electrolyte containing 10 mmol of Bu_4N^+, the data of Table 1 would suggest that the concentration of $ZnCl_4^{2-}$ in the methylene chloride will be about 0.04 mol dm^{-3}. This might be sufficient to maintain the flux of nucleophile necessary to give a good selectivity of product at a current density of 50 mA cm^{-2} with efficient stirring in the electrolysis cell. On increasing the current density to 150 mA cm^{-2}, however, the selectivity drops from 74 to 43% although it recovers to 64% on trebling the concentration of phase transfer reagent.

Table. 4. Effect of current density and concentration of Bu_4N^+ on the electrolysis. Electrolysis conditions: 0.1 mol $C_{10}H_8$ in 100 cm^3 $C_{10}H_8$ + 0.15 mol $ZnCl_2$, 0.3 mol NaCl, 9 g Na_2SO_4 and Bu_4NHSO_4 in 100 cm^3 H_2O. Undivided cell with Pt anode and Ni cathode. Electrolyses terminated after 2.33 F mol^{-1} $C_{10}H_8$

I(mA cm^{-2})	Bu_4N^+ (mmol)	$C_{10}H_8$ consumed (%)	Selectivity $C_{10}H_7Cl$ (%)
50	10	58	74
130	10	61	43
	20	64	59
	30	71	64

The use of a Ti/RuO_2 instead of a Pt anode leads to some loss of selectivity but the major result of this change of anode is to reduce the consumption of naphthalene, i.e. the current efficiency, see Table 5. This may well be due to increased chlorine evolution although such a change of product would have to result from inhibition of naphthalene oxidation at the RuO_2 surface rather than improved catalysis of chlorine evolution since the I–E curves show that even at Pt, the oxidation of $ZnCl_4^{2-}$ is mass transport controlled at the potential where the hydrocarbon oxidizes.

Table 5. Comparison of Ti/RuO_2 and Pt as anodes. Other electrolysis conditions: 10 mmol $C_{10}H_8$ in 100 cm^3 CH_2Cl_2 + 0.15 mol NaCl, 9 g Na_2SO_4 and 10 mmol Bu_4NHSO_4 in 100 cm^3 H_2O. Electrolyses terminated after 2.33 F mol^{-1} $C_{10}H_8$.

Anode	I (mA cm^{-2})	$C_{10}H_8$ consumed (%)	Selectivity $C_{10}H_7Cl$ (%)
Pt	50	60	74
Ti/RuO_2	50	27	61
	80	36	47

Table 6. Comparison of data from undivided and divided cells. Electrolysis conditions for divided cell: Anolyte was 0.06 mol $C_{10}H_8$ in 60 cm^3 CH_2Cl_2 + 0.09 mol $ZnCl_2$, 0.18 mol NaCl, 5 g Na_2SO_4 and 6 mmol Bu_4NHSO_4 in 60 cm^3 H_2O. Catholyte only $ZnCl_2$ + NaCl in H_2O. Undivided cell conditions as Table 3. $I = 50$ mA cm^{-2}

Cell type	Charge ($F\,mol^{-1}$)	$C_{10}H_8$ consumed (%)	Selectivity (%)	
			$C_{10}H_7Cl$	$C_{10}H_6Cl_2$
divided	1.0	47	69	0
	2.5	87	90	10
undivided	1.0	36	53	0.4
	2.33	55	83	4

Table 6 compares data for the electrolysis in both undivided and divided cells. It can be seen that the selectivity is slightly higher in the divided cell but the larger effect is on the conversion of naphthalene and hence current efficiency. Figs 1 and 2 show data from further experiments in the two cells; in these experiments, the electrolyses were continued until much higher charges had been passed and the progress of the process was monitored at intervals. The dichloronaphthalene, whose exact structure was not determined, can clearly be seen to be the product of further oxidation of 1-chloronaphthalene. Comparison of the two curves again shows that the electrolysis proceeds more rapidly in the divided cell and the maximum yield of 1-chloronaphthalene, and probably dichloronaphthalene, is also higher in this cell.

In the experiment reported in Fig. 3, the conversion of naphthalene to 1-chloronaphthalene has been followed during the early stages of the electrolysis. Also shown in the figure is the amount of starting material unaccounted for after the determination of both naphthalene and chloronaphthalene. It can be seen that this curve peaks at about 1 F mol^{-1} and by 2 F mol^{-1} effectively all the material is accounted for. Moreover it was observed that the organic phase went from colourless to a red pink colour around 1 F mol^{-1} and then turned yellow as the electrolysis continued. It was noted earlier that a low selectivity at 1 F mol^{-1} has been found in many experiments, e.g. see Tables 3 and 6. Even so, some consideration has been given to the possibility that this observation is the result of a systematic analytical error. This appears not to be the case since analysis was car-

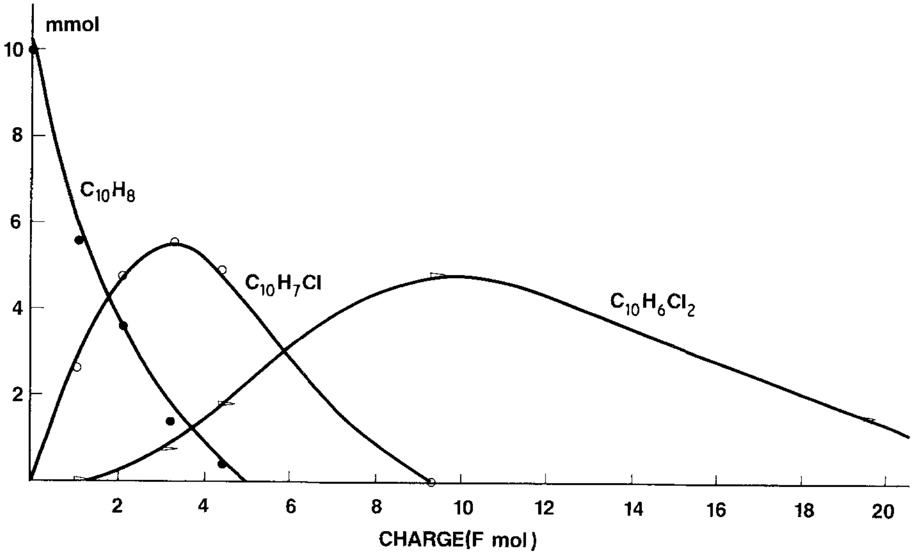


Fig. 1. Conversion of naphthalene to chlorinated products as a function of charge passed in the undivided cell. The electrolyte was 10 mmol of $C_{10}H_8$ in 100 cm^3 CH_2Cl_2 + 0.15 mol $ZnCl_2$, 0.3 mol NaCl, 9 g Na_2SO_4 and 10 mmol Bu_4NHSO_4 in 100 cm^3 H_2O. $I = 50$ mA cm^{-2}.

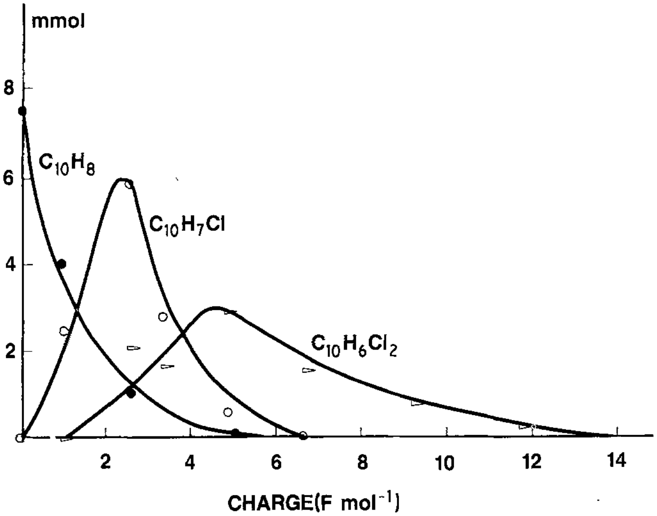


Fig. 2. Conversion of naphthalene to chlorinated products as a function of charge passed in the divided cell. The anolyte was 7.5 mmol of $C_{10}H_8$ in 75 cm^3 CH_2Cl_2 + 0.12 mol $ZnCl_2$, 0.24 mol NaCl, 6 g Na_2SO_4 and 7.5 mmol Bu_4NHSO_4 in 75 cm^3 H_2O. The catholyte was aqueous NaCl + $ZnCl_2$. $I = 50\,\mathrm{mA\,cm^{-2}}$.

ried out both by direct glc analysis of the methylene chloride phase during electrolysis and by sampling and extraction of the organic product before glc analysis. Hence we conclude that a metastable intermediate is present during the electrolysis.

5. Discussion

The results described in the previous section confirm the advantage of carrying out the conversion of naphthalene to 1-chloronaphthalene using the complex anion, $ZnCl_4^{2-}$, rather than chloride ion as the nucleophile (although both are present in the organic phase largely as ion aggregates). Moreover, the data show the two phase procedure described to be a good synthetic method. The electrolysis can be carried out with a high concentration of starting material and at a reasonable current density using very simple cell designs; the best conditions give a selectivity of about 90% with a current efficiency of nearly 80%. In comparing these figures with those obtained when chloride ion [1, 2] is the anion transferred, three factors seem to be particularly important: (i) the presence of zinc ion in the system, principally, improves the selectivity of the reaction and largely this is achieved by reducing the amount of naphthalene consumed, cf. Figs 1 and 2, (ii) the ratio of naphthalene to $ZnCl_4^{2-}$ (or its ion aggregate) concentrations in the methylene chloride is important, (iii) the greatest improvement in current efficiency occurs as a result of using a divided cell; this would suggest that transport of material between electrodes is disadvantageous and the low current efficiency in the undivided cell is not entirely due to competing reactions at the anode. It is possible that zinc powder could dechlorinate 1-chloronapthalene to naphthalene under some conditions, but with a Ni cathode the major reaction is, however, H_2 evolution and little zinc powder can be formed.

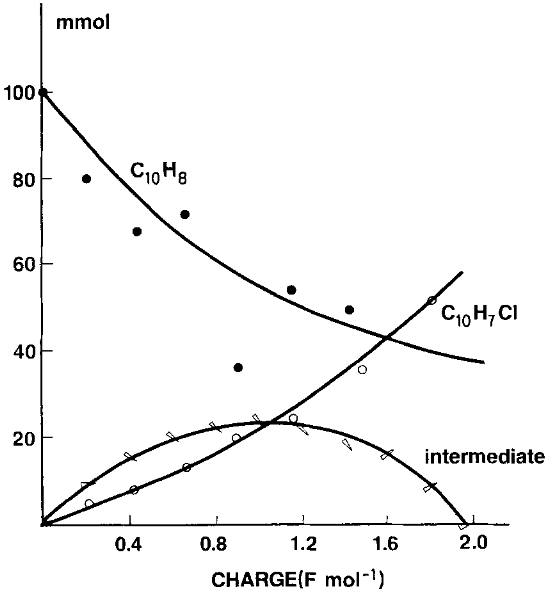
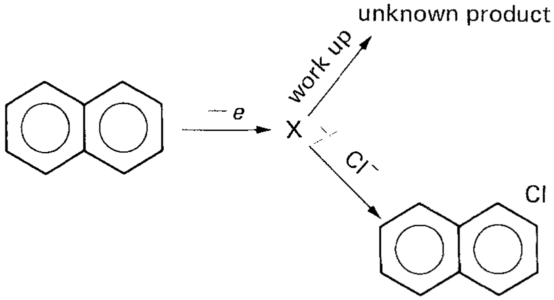


Fig. 3. Conversion of naphthalene to 1-chloronaphthalene and unknown intermediate as a function of charge passed in the undivided cell. Electrolyte and other conditions as Fig. 1 except the naphthalene used was 100 mmol.

In experiments where the reaction is monitored as a function of conversion, the results seem to implicate a stable intermediate during the early stages of the electrolysis. This intermediate, if indeed present, must be capable of forming 1-chloronaphthalene or an alternative product, not visible by glc analysis, during work-up of the electrolyte, i.e.



Fritz and coworkers have described the isolation of dark red, dimeric cation radical salts of naphthalenes [3, 4]. Such a species would explain many of our observations including the variation in the importance of the intermediate as a function of charge passed and the colour changes; the formation of a dimer cation radical requires the presence of unoxidized naphthalene. On the other hand, the dimer cation radical may not have any stability in the presence of water and oxygen at room temperature. Nor could we record a convincing esr spectrum for the organic phase when the electrolysis was terminated after 1 F mol^{-1}.

The mechanism by which the zinc ion improved the selectivity of the anodic chlorination of naphthalene in these two phase systems is still not completely clear. Several possibilities can, however, be completely ruled out. Certainly despite the fact that the chloride ion is complexed by zinc, naphthalene is still more difficult to oxidize than the free chloride in the system. This is in contrast to earlier studies [5] where the addition of $AlCl_3$ to the chloride ion in acetonitrile shifted the oxidation of the chloride to very positive potentials. Similarly a positive role for the cathode can be ruled out since better results were obtained in a divided cell. Overall, it seems most likely that the zinc species stabilizes an intermediate and/or an aromatic species in the system and prevents polymerization of the hydrocarbon and/or reaction of cationic intermediates with water to form naphthols, naphthaquinones etc. For example, the dimer cation radical of naphthalene may complex with $ZnCl_4^{2-}$ or zinc ion in an ion aggregate and reduce its tendency to take part in unwanted side reactions. Whether this stabilization results from direct complexation of the aromatic compound by the zinc (II) or is an indirect effect resulting from less water at the site of interaction of cation radical and nucleophile cannot yet be said with certainty. The former is perhaps more convincing.

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