JOURNAL OF APPLIED ELECTROCHEMISTRY 12 (1982) 687–691

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

I. The anodic cyanation of naphthalene

S. R. ELLIS, D. PLETCHER

Department of Chemistry, The University, Southampton SO9 5NH, UK

P. GOUGH, S. R. KORN

The Heavy Chemicals New Science Group, ICI Ltd, PO Box 8, The Heath, Runcorn, Cheshire, WA7 4QD, UK

Received 18 March 1982

The anodic cyanation of naphthalene in a methylene chloride/water emulsion using a phase transfer catalyst to supply cyanide ions to the organic medium has been re-examined. The effect of electrolysis parameters (e.g., current density, electrode material, concentration of cyanide, naphthalene and phase transfer catalyst) on the current and organic yields of products is reported. It is shown that by correct selection of conditions it is possible to improve substantially on the yields reported in the literature; the organic and current yields of 1-cyanonaphthalene can exceed 80% and 65%, respectively.

1. Introduction

The anodic substitution of aromatic molecules in aprotic solvents has been widely studied [1–3]. In general, while a number of interesting reactions have been shown to be possible, the yields are poor; problems arise because the monosubstituted derivatives are more readily oxidized than the starting materials or because the anode reaction also produces protons, a rather reactive species in such solvents. Moreover, the need for pure, dry solvents and expensive quaternary ammonium salts, the high energy consumption (aprotic solvents have a high resistitivity) and the decomposition of the solvent/electrolyte at the cathode all militate against their use. In 1974, Eberson and Helgee [4] described a new procedure involving the electrolysis of two immiscible solvents, methylene chloride containing the substrate (naphthalene) and water containing sodium cyanide, in the presence of a phase transfer agent, tetrabutylammonium ions (in the form of the relatively cheap bisulphate salt). They demonstrated a typical current yield of 34% (organic yield 51%) of 1-cyanonaphthalene and later showed that the method was also applicable to the cyanation of other aromatic substrates [5–7].

The principle of this type of two-phase electrolysis is illustrated in Fig. 1 where it can be seen that the anode reaction occurs in the organic solvent but the nucleophile is supplied by transfer of an ion pair, $[Bu_4N^+CN^-]$, from the aqueous solution. Moreover such electrolyses seem worthy of more detailed study since they have a number of potential advantages. Namely, (a) the nucleophile can come from a very cheap source, e.g., Na^+X^-, (b) the aqueous solution may be used to buffer the organic phase, (c) the cathode process can be a very clean reaction, hydrogen evolution, (d) the isolation of the product requires the work up of only the methylene chloride phase, (e) reduced energy consumption compared to an aprotic electrolysis since much of the inter-electrode gap is filled by aqueous electrolyte, Eberson and Helgee [4] claimed a 4–18 fold decrease in cell voltage. Hence a series of papers will report a detailed investigation of several aspects of this type of two-phase electrolysis. This first paper deals with the effects of electrolysis parameters (e.g., conversion, current density, concentrations

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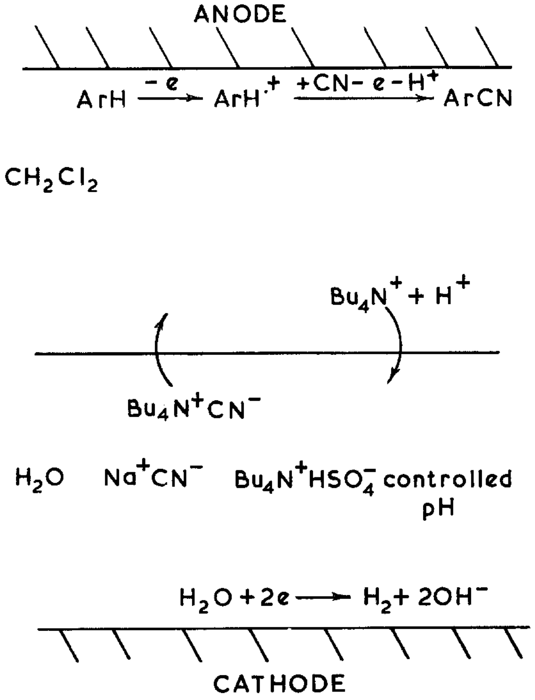

Fig. 1. Schematic representation of anodic nucleophilic substitution by two-phase electrolysis.

of substrate and electrolytes) on the yields for the cyanation of naphthalene and it will be shown that it is possible to improve substantially on those reported in the literature. Later papers will report on other substitution reactions and on approaches to the scale-up of such electrolyses.

2. Experimental procedure

All electrolyses were carried out at constant current using an enclosed beaker-type cell. In general, the anode was a 50 cm^2 Pt sheet, the cathode a similar sized steel gauze and the emulsion was formed and maintained with an air-powered PTFE paddle stirrer rotated at 450 rpm. Particular experiments required obvious modification of this cell.

In a typical electrolysis procedure 100 cm^3 of aqueous tetrabutylammonium bisulphate were neutralized by NaOH and adjusted to pH 12 before the addition of the NaCN. The naphthalene and a known quantity of hexadecane (internal standard) were dissolved in 100 cm^3 of methylene chloride. The filled cell was immersed in an ice/water bath and the stirrer was switched on to form the emulsion; the electrolysis was carried out at constant current, obtained from a Bank Elektronik LB75H potentiostat or a KSM stabilized power supply, until a predetermined charge (checked with a laboratory built integrator) had been passed. The phases were then allowed to separate and the organic phase was analysed by gas–liquid chromatography (glc) using a Pye Unican GCD chromatograph and an OV 17 column (N_2 carrier gas 60 cm^3 min^{-1}, column temperature (130° C). Products were identified and estimated by comparison of retention times and peak areas with those for standard solution of authentic samples.

The chemicals used were the purest available.

3. Results

In these two-phase anodic substitution reactions, there is a large number of experimental parameters which would be expected to effect the yield of the products. Those considered in this study of the cyanation of naphthalene were the anode material, anode current density, organic solvent, temperature, type of phase transfer agent, the concentrations of naphthalene, cyanide ion and phase transfer agent, pH, percentage conversion and the stirring regime used to form and maintain the emulsion.

The number of variables to be investigated in detail was, however, somewhat reduced in a preliminary study using conditions close to those recommended by Eberson and Helgee [4]. Firstly the choice of both the electrode material and the organic solvent was shown to be critical. Using methylene chloride as the solvent, the yield of cyanonaphthalene was found to be acceptable (organic yield 40–50%, current yield 30–35%) using either a platinum or a platinized titanium anode but when the anode was carbon, lead dioxide or ruthenium dioxide/titanium the current yields were very low (< 5%). The choice of solvent is also limited since the organic solvent must be a reasonable medium for electrochemistry (e.g., no reaction was obtained using toluene, carbon tetrachloride or fluorocarbons as the solvent). Moreover, since the solvent must be immiscible with the aqueous solution, the only solvents which could be used successfully were methylenedichloride and nitrobenzene. The former was considered the better choice for preparative electrolyses solely

Table 1. Effects of reactant concentrations on the products of electrolysis. Electrolysis conditions: 100 cm^3 water containing Bu_4NHSO_4 neutralized with NaOH, NaCN and saturated Na_2SO_4 and 100 cm^3 methylenedichloride containing naphthalene stirred with propeller blade rotating at 450 rpm. Anode current density 20 mA cm^{-2}. Charge passed ≡ 4 F mol^{-1} naphthalene

Amount of reactants (mol)			*Product distribution* (% initial $C_{10}H_8$)		
NaCN	Bu_4N^+	$C_{10}H_8$	$C_{10}H_8$	$C_{10}H_7CN$ + *isomers (ratio 1:2)*	*polymer*
0.31	0.01	0.1	17	22 (21:1)	53
–	–	0.02	8	54 (5:1)	34
–	–	0.004	7	57 (7:1)	20
0.06	0.01	0.02	11	57 (5:1)	25
0.06	0.03	0.02	14	85 (5:1)	0

because of the difficulty in removing the higher boiling point solvent after electrolysis.

A literature survey [8–10] indicated that a wide range of phase transfer reagents should have been applicable. In fact, a series of experiments was carried out where an aqueous solution (0.6 mol dm^{-3} NaCN + 0.1 mol dm^{-3} NaOH + 0.1 mol dm^{-3} R_4NHSO_4) was equilibrated with methylene chloride and the phases analysed showed that $(CH_3)_4N^+$ and $(C_2H_5)_4N^+$ were ineffective for the transfer of cyanide ion; with $(C_4H_9)_4N^+$, 98% of the organic cation transferred as the cyanide but with $(C_6H_{13})_4N^+$ this figure was diminished because transfer of bisulphate was also observed. Hence the tetrabutylammonium ion was used as the phase transfer agent and the bisulphate was employed since it was the cheapest salt available. The yield of product was, however, insensitive to the electrolysis temperature in the range 270 to 315 K.

As a result all later electrolyses were carried out at ambient temperature and used a platinum (or occasionally Pt/Ti) anode and a water/methylenedichloride emulsion containing tetrabutylammonium bisulphate. The aqueous phase was always neutralized with caustic soda prior to addition of sodium cyanide (to avoid HCN) and also saturated with sodium sulphate to enhance the transfer of cyanide to the organic solvent.

Table 1 reports the product distribution from a series of electrolyses where the reactant and catalyst concentrations were varied. At the highest naphthalene concentration investigated (1 mol dm^{-3}) polymer was the major product but its yield drops as the naphthalene concentration is reduced. At the same time the yield of cyanonaphthalene increases but when the concentration of tetrabulyammonium ion is 0.1 mol dm^{-3} the conversion at 4 F mol^{-1} plateaus at 57%. It could, however, be increased further up to 85% (and an almost quantitative organic yield) by increasing the amount of phase transfer catalyst by a factor of three. The sodium cyanide concentration in the aqueous phase did not affect the yield of cyanonaphthalene provided it was present in excess of the tetrabutylammonium ion. It is likely that the cyanonaphthalenes are formed by the initial oxidation of naphthalene to its cation radical followed by nucleophilic attack by cyanide ion. It is therefore not surprising that the yield of substituted product is dependent on the ratio of the naphthalene and cyanide ion concentrations in the organic phase and the optimum seems to arise from a 3:2 ratio of $(C_4H_9)_4N^+$: $C_{10}H_8$.

Fig. 2 summarizes the results of an experiment where the concentrations of reactant and products were monitored during an electrolysis run under the best conditions from Table 1. It can be seen that throughout the electrolysis, all the naphthalene consumed is converted to cyanonaphthalene but the current yield is highest during the first half of the electrolysis. In fact the current yield averages 67% up to 1.5 F mol^{-1} and thereafter drops reaching an overall value of 42% after 4 F mol^{-1}. Hence it is clearly advantageous to the energy consumption to terminate the electrolysis at about 50% conversion.

The data from a series of electrolyses at different current densities is reported in Table 2. The yield of cyanonaphthalene does not vary with current density in the range 20–80 mA cm^{-2} but the current efficiency of the electrolyses drops

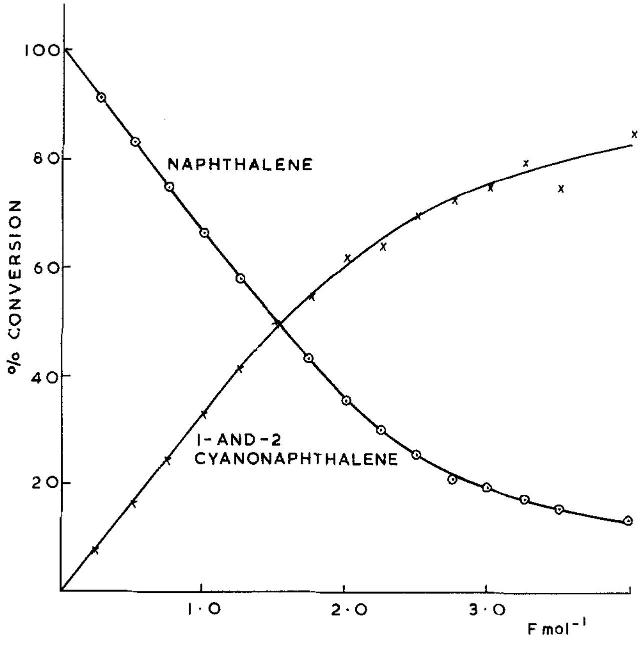

Fig. 2. Analysis of the methylene chloride phase as a function of charge passed. Electrolysis conditions: 100 cm^3 H_2O saturated with Na_2SO_4 and containing Bu_4NHSO_4 (0.03 mole) neutralized with NaOH and NaCN (0.06 mole) + 100 cm^3 methylene chloride containing $C_{10}H_8$ (0.02 mol). $I = 20$ mA cm^{-2}. Stirrer speed 450 rpm.

slightly at the higher current density. The stirring regime was also found to have little effect on the electrolysis performance; cells were constructed with a variety of vertical gauze and sheet electrodes and either the anode or cathode was rotated. The results are summarized in Table 3 while Fig. 3 illustrates the effect of the stirring rate using the example of a rotating steel mesh cathode. With all the cells investigated the percentage conversion (and current yield) increased slightly with stirring rate until a critical value, above which the percentage conversion became independent of the stirring rate. Moreoever, the critical rotation rate is quite modest.

Table 2. Effect of anode current density on the yields of cyanonaphthalenes. Electrolysis conditions: 100 cm^3 H_2O containing NaCN (0.06 mole) and Bu_4NHSO_4 (0.03 mole) neutralized with NaOH and saturated with Na_2SO_4 + 100 cm^3 CH_2Cl_2 containing $C_{10}H_8$ (0.02 mole). Stirrer rate 450 rpm. 2.5 F mole^{-1}.

I (mA cm^{-2})	*Yields of cyanonaphthalene*		
	Organic yield (%)*	*current yield (%)*	*Ratio of 1:2 isomer*
20	79	61	5:1
40	78	56	8:1
60	75	57	7:1
80	74	52	7:1

* Based on naphthalene consumed.

Hence it is the conclusion of this study that very high organic yields of 1-cyanonaphthalene (> 80%) can be obtained and that the current yield can be as high as 65% if the electrolysis is terminated at 50% conversion. Moreover, such results can be achieved over a wide range of temperature, current density and stirring regime although the selection of solvent and anode material is important and the concentration of the tetraalkylammonium ion and the naphthalene must be carefully controlled. Moreover the yields obtained here are much higher than those obtained by one-phase electrolysis [11, 12]. The high organic yield is maintained to high conversion because the cyanated product is stable to further oxidation. On the other hand, the current yield decreases as the naphthalene concentration drops because other anode reactions become more favourable.

The mechanism of two-phase anodic substitution will be discussed in later papers but the study of the mechanism of the cyanation of naphthalene is hampered by our inability to obtain good quality *I–E* curves for the oxidation of cyanide in methylene chloride. It is probable, however, that cyanide is oxidized at less positive potentials than naphthalene, in which case the formation of cyanonaphthalene in good yields is dependent on the flux of cyanide to the anode surface being met

Table 3. Effect of stirring on the cyanation of naphthalene. Other conditions as Table 2

Cell	*Cyanonaphthalene*	
	Percentage conversion	*Current efficiency (%)*
1. Pt sheet anode, steel gauze cathode stirrer* (0.7 or 2.5 mm mesh)	66	53
2. Pt sheet anode stirrer,* steel gauze cathode	53	42
3. Pt/Ti gauze anode stirrer,* (5 mm mesh) steel gauze cathode	65	52
4. Pt sheet anode, steel gauze cathode, PTFE blade stirrer*	70	56
5. Pt sheet anode, steel gauze cathode, Ultra Turrax stirrer	67	53

*600 rpm.

by a flux of naphthalene cation radicals away from the surface so that no cyanide ions reach the surface. Indeed as the naphthalene concentration drops, the current probably goes into cyanide oxidation because the flux of cation radicals becomes insufficient to mop up all the incoming cyanide ions. Another interesting feature of two-phase electrolysis is the possible role of a continuous organic solvent film over the anode surface. Two observations particularly point to the essential presence of such a film; the strong dependence on anode material (cf., one-phase electrolysis where C and Pt would be interchangeable) and the low extent of water oxidation which would also be expected to be thermodynamically favourable compared to naphthalene oxidation.

Acknowledgement

This research programme was fully supported by ICI Ltd under its Joint Research Scheme.

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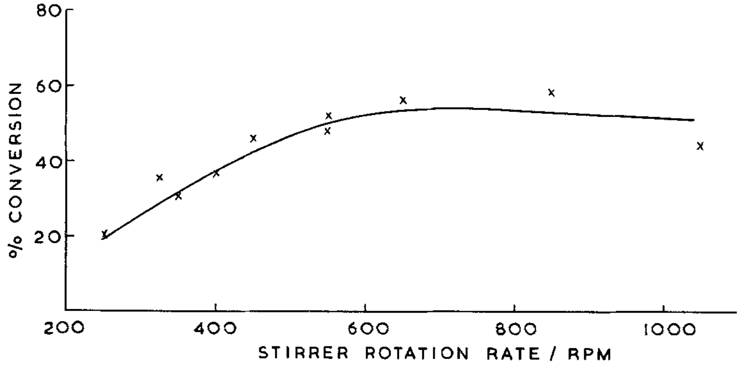

Fig. 3. Percentage conversion of naphthalene to cyanonaphthalene after 2.5 F mol^{-1} as a function of rotation rate of a 1.25 mm stainless steel mesh cathode/stirrer. Other conditions as for Fig. 2.