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SHORT COMMUNICATION

Electrochemical thiocyanation by two phase electrolysis

P. KRISHNAN, V. G. GURJAR*

Department of Chemical Engineering, Indian Institute of Technology, Powai, Bombay, 400 076, India

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1. Introduction

Thiocyano derivatives of organic compounds are used as intermediates for preparing dyes, insecticides and a large variety of compounds [1, 2]. Since chlorine and bromine are used as oxidizing agents in chemical thiocyanation, the handling and storage of these and the formation of halo substituted side products are the difficulties involved in chemical thiocyanation.

The electrochemical method has been employed for the preparation of thiocyano derivatives of many organic compounds [3]. Since thiocyanogen, $(SCN)_2$, the thiocyanating reagent produced during electrolysis, is highly unstable in aqueous solutions [4], electrolyses have to be carried out mainly in nonaqueous solvents [5, 6]. Electrolysis in nonaqueous solvents has inherent disadvantages, such as poor solvent conductivity and the need for highly expensive supporting electrolyte salts. Moreover, water itself is needed for the counter electrode reaction. Therefore, electrolysis of a mixed solution containing both the aqueous and the nonaqueous phase is preferred to electrolysis in homogeneous nonaqueous solvents.

Two phase electrochemical synthesis has been successfully employed for substitution, as well as oxidation, reactions of electrochemically prepared molecular halogens [7–9]. In this paper, the two phase electrolysis method has been studied for thiocyanation reactions using 2-methylphenol (*o*-cresol) as the model compound.

2. Experimental details

All the experiments were carried out in an undivided cylindrical cell of capacity 200 ml. The cell had a Teflon cover with openings to fix the electrodes, the Luggin capillary and a thermometer. All the chemicals were of AR grade and were used as received. The aqueous solutions were prepared with double distilled water. A magnetic stirrer was employed during polarization measurements as well as two phase electrolyses. The experiments at low temperature were carried out by placing the cell in a bath through which ethylene glycol was circulated from a cryostat to maintain the required temperature.

2.1. *Polarization measurements*

The working electrode for the polarization studies was a graphite plate of area $10\,cm^2$ and another graphite electrode was the counter electrode. All the measurements were carried out with respect to a saturated calomel electrode (SCE) at room temperature (25 °C).

An EG&G PARC potentiostat (Model 273) interfaced to an IBM PC was used for the measurements. The current potential curves were recorded at a scan rate of $5\,mV\,s^{-1}$.

2.2. *Preparative scale experiments*

Preparative scale electrolyses were carried out using three rectangular graphite plate electrodes (geometrical area $20\,cm^2$). One anode and two cathodes were fixed with an inter electrode distance of 3 mm. The solution contained 65 ml aqueous solution of 2 M NH_4SCN in 0.5 N H_2SO_4 and 65 ml of dichloromethane (CH_2Cl_2) with the substrate 2-methylphenol dissolved in it. Constant current electrolysis was carried out with a stabilised d.c. power supply (4 A, 10 V) at 0 °C.

After completion of the electrolysis, the two phases were separated and the aqueous phase was washed with 25 ml of dichloromethane and the washings were added to the organic phase. The organic phase was stirred overnight to ensure completion of the substitution reaction. It was then dried with anhydrous sodium sulphate and the solvent was removed over a water bath. The product was purified over a silica gel column using petroleum ether-ethyl acetate (10 : 1) as eluent. It was characterized by infrared and NMR spectral techniques.

3. Results and discussion

3.1. *Current potential curves*

It can be seen from Fig. 1 (curves a and b) that oxygen evolution is the main reaction on the graphite anode in the aqueous sulphuric acid medium, as well as in the two phase system, at potentials higher than 1.3 V. The substrate 2-methylphenol undergoes facile oxidation at the anode when present in sulphuric acid solution (curve c). However, no current corresponding to the oxidation of the substrate is observed in the two phase system and only oxygen evolution occurs beyond 1.3 V (curve d). In the two phase system, oxidation of 2-methylphenol at the anode is prevented because it is exclusively present in the nonconducting organic phase.

The polarization curve for the two phase system containing thiocyanate is similar to that for the aqueous thiocyanate solution with the oxidation of thiocyanate commencing at 0.450 V against SCE on the graphite

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*Author to whom all correspondence should be addressed.

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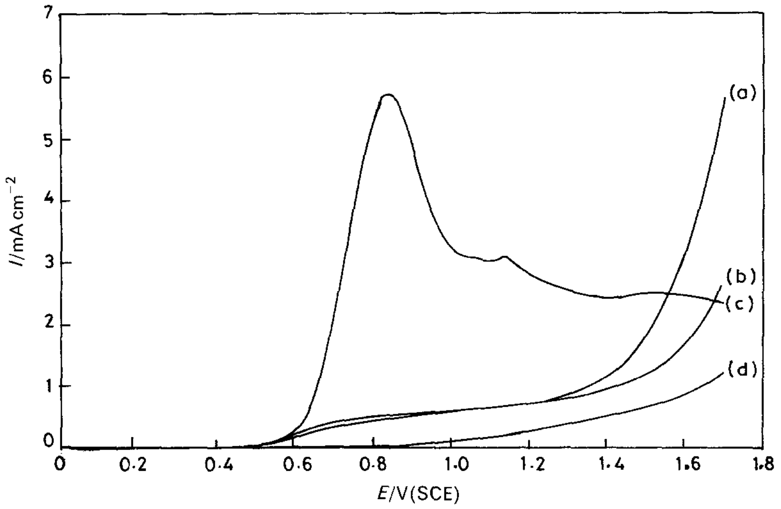

Fig. 1. Polarization curves: (a) 0.5 N H_2SO; (b) two phase system of 0.5 N H_2SO_4 (65 ml) and CH_2Cl_2 (65 ml); (c) 13 mmol 2-methylphenol in 0.5 N H_2SO_4 (130 ml); (d) 13 mmol 2-methylphenol in 0.5 N H_2SO_4(65 ml) + CH_2Cl_2 (65 ml).

electrode. It has already been reported that trithiocyanate $(SCN)_3^-$ is the species produced in acidic solutions [10]. In the two phase media, the trithiocyanate formed in the aqueous electrolyte may dissociate to produce thiocyanogen and thiocyanate [11] resulting in thiocyanogen entering into the nonaqueous phase, thereby, preventing its decomposition in the aqueous phase. The homogeneous substitution reaction between the substrate and thiocyanogen then occurs in the organic phase.

3.2. *Preparative electrolysis*

Preliminary experiments were carried out without the organic substrate to establish the favourable experimental conditions for the preparation of the thiocyanating species by two phase electrolysis. The same experimental conditions were employed for the preparative scale electrolyses. The only product obtained during the substitution reaction was 2-methyl-4-thiocyanophenol. The presence of the thiocyano group in the product was identified by the characteristic sharp peak around 2170 cm^{-1} [1], in the i.r. spectrum. The structure of the product was confirmed by the following NMR spectral data. ^{1}H NMR($CDCl_3$, 300 MHz), δ 2.25 (s, 3H, CH_3), 5.50 (brs, 1H, OH), 6.80 (d, 1H, $J_{6\text{-}5}$ = 8.39 Hz, H-6), 7.28 (dd, 1H, $J_{5\text{-}6}$ = 8.39 Hz, $J_{5\text{-}3}$ = 2.3 Hz, H-5), 7.35 (d, 1H, $J_{3\text{-}5}$ = 1.83 Hz, H-3).

The results of preparative electrolyses for various durations are given in Table 1. It is evident from the table that the current efficiency remains almost constant for all the electrolysis durations studied. It was observed that the product was precipitated in the organic phase when more than 10 mmol of the substrate was employed for the reaction. However, precipitation of the product was not found to affect the current efficiency.

*Table 1. The current efficiency for thiocyanation of 2-methylphenol at various electrolysis durations**

No.	Electrolysis duration/h	2-methyl phenol/mmol	2-methyl-4-thio cyanophenol/mmol	Current efficiency/%
1	2	7.5	4.5	59
2	3	11.4	5.5	50
3	4	15.4	6.4	43
4	5	18.5	10.2	55

* Current density: 10 mA cm^{-2}; electrolyses terminated after 2 F mol^{-1} of substrate.

Current densities from 5–150 mA cm^{-2} were examined and the variation of current density was not found to affect the current efficiency of the process. The electrolysis can be carried out at a current density of as high as 150 mA cm^{-2}. Thiocyanate oxidation requires high overvoltage of around 0.5 V at graphite electrode. Electrolysis at higher current densities is not possible in homogeneous nonaqueous solvents since the organic substrate also undergoes simultaneous oxidation with the thiocyanate. Hence, electrolysis at the higher current densities is possible only with the two phase electrolysis method.

Electrolyses at higher current densities and electrolyses for longer durations without loss in current efficiency are possible with high concentrations of thiocyanate in the aqueous phase.

The percentage material yield was calculated for various quantities of charge and it was found that four Faradays per mole are needed for the quantitative conversion of the reactant into its thiocyano derivative. In all cases, a part of the reagent underwent polymerization in the organic phase when stirred at ambient temperature for completion of the substitution reaction. As reported in the literature [1], the slower rate of reaction of the phenols with the thiocyanating reagent is the cause for its polymerization, which in turn lowers the current efficiency for the process. The possibility of part of the reagent undergoing decomposition in the aqueous phase before its extraction into the nonaqueous phase may also be a reason for the low current efficiency of the process.

The various reactions occurring during two phase electrolysis are

$$3SCN_{aq}^- - 2e^- \longrightarrow (SCN)_3^- \text{ (aq)}$$

$$(SCN)_3^- \text{ (aq)} \rightleftharpoons (SCN)_2 \text{ (aq)} + SCN^- \text{ (aq)}$$

$$(SCN)_2 \text{ (aq)} \longrightarrow (SNC)_2 \text{ (org)}$$

$$(SCN)_2 \text{ (org)} + \text{R–H (org)} \longrightarrow \text{R–SCN (org)} + SCN^- + H^+$$

where R–H denotes the substrate.

The advantage of this two phase electrochemical method is that it can be employed for thiocyanation of all types of substrates which react with thiocyanogen. The electrochemical preparation of the thiocyanating reagent and its substitution reaction can be carried out either *in situ*, as in the present study, or in two separate steps depending on the nature of the substrate. The two step method has been successfully employed for thiocyanation of various amines and phenols [12].

4. Conclusions

The two phase electrochemical thiocyanation of 2-methylphenol without its simultaneous oxidation is possible because of the substitution reaction occurring in the nonconducting organic phase.

A current efficiency of about 50% can be obtained for the preparative electrolyses. Two phase electrolysis can be carried out at a current density of 150 mA cm^{-2}. Quantitative conversion of the substrate is possible by passing four Faradays of electricity per mole of reactant.

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