JOURNAL OF APPLIED ELECTROCHEMISTRY **18** (1988) · SHORT COMMUNICATION

SHORT COMMUNICATION

Chlorination of toluene by two-phase electrolysis

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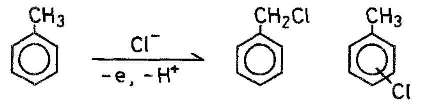
Received 16 June 1987

1. Introduction

The electrochemical chlorination of aromatic compounds is of interest from two standpoints; the development of new practical processes and understanding the mechanism of many electrochemical oxidations. The electro-chlorination of toluene has been attempted by many workers. Gourcy *et al.* [1], for instance, carried out the anodic chlorination of toluene in CH_3CN containing some Lewis acids and obtained *o*- and *p*-chlorotoluenes. We [2] have also obtained chlorotoluenes with high yields through the electrolysis of toluene in $CH_3OH/LiCl$. However, no chloroderivatives substituted in the methyl group have been reported as formed by electrochemical methods. Forsyth and Pletcher [3] have discussed 'two-phase electrolysis' as an advantageous technology in practical organic electrosynthesis. However, we wish to show that two-phase electrolysis can yield different products from conventional homogeneous electrolysis. In the present work, we have obtained benzyl chloride as well as chlorotoluenes by the electrolysis of toluene in immiscible two-phase systems (Scheme 1).



Scheme 1.

2. Experimental details

A beaker-type glass cell was used for the electrolysis. The anode was a Pt wire ($2.9\,cm^2$) and the cathode was a Pt sheet ($5.4\,cm^2$). The aqueous phase of the electrolytic solution was $12\,mol\,dm^{-3}$ HCl ($40\,cm^3$) which acted as a supporting electrolyte and a Cl^- source. The organic phase consisted of $40\,cm^3$ benzene (C_6H_6) or dichloromethane (CH_2Cl_2) containing 5×10^{-3} mol of substrate toluene. Neat toluene ($40\,cm^3$) was also used as the organic phase. The electrolysis was conducted galvanostatically (current: 50 mA) either with vigorous stirring of the solution (emulsion electrolysis) or without stirring, i.e. leaving the immiscible phases separated (stationary electrolysis). In some experiments, a 15 W fluorescent lamp was used as a light source. The product analyses were carried out by gas chromatography.

3. Results and discussion

Table 1 shows the results of the chlorination by two-phase electrolysis. The amount of electricity passed (965 C) was equivalent to that required for a 2-*e* oxidation of the toluene (5×10^{-3} mol) in the system. In the emulsion system (Runs 1–3 and 7) the main products were *o*- and *p*-chlorotoluenes. The product yields, or the current efficiency, tended to increase with the electrolyte temperature. On the other hand, the stationary electrolysis (Runs 4–6) mainly yielded benzyl chloride. Indeed, the use of benzene as the solvent gave benzyl chloride only. The electrolyses without solvents (Runs 6 and 7) improved the total yields of the products, but lowered the selectivity in the stationary system (Run 6). The *o*-/*p*- ratio of chlorotoluenes was about 2 in every case. The irradiation with fluorescent light assisted the formation of benzyl chloride both in the stationary and emulsion systems. Other factors affecting the product yields, such as the current density, the amount of electricity passed and pH of the aqueous phase, were also examined. The results led to the following conclusions concerning the reaction mechanisms. The electro-chlorination is

Table 1. Results of anodic chlorination of toluene by two-phase electrolysis

Run	*Solvent*[a]	*System*[b]	*Light*[c]	*Temp.* (°C)	*Yield*[d] (%)			
					o-*CT*	p-*CT*	*BC*	*Total*
1	CH_2Cl_2	E	no	25	26.0	13.6	trace	39.6
2	CH_2Cl_2	E	no	4 ± 2	10.9	6.6	5.8	23.3
3	C_6H_6	E	no	7 ± 2	5.8	2.7	trace	8.5
4	CH_2Cl_2	S	yes	4 ± 2	trace	trace	5.8	5.8
5	C_6H_6	S	yes	4 ± 2	–	–	18.8	18.8
6	–	S	yes	4 ± 2	17.7	8.3	25.6	51.6
7	–	E	no	25	55.4	26.4	–	81.8

[a] Runs 1–5: $12\,mol\,dm^{-3}$ HCl ($40\,cm^3$)/solvent + 0.005 mol toluene; Runs 6 and 7: $12\,mol\,dm^{-3}$ HCl ($40\,cm^3$)/toluene ($40\,cm^3$).

[b] E: In emulsion system, S: in stationary system (see text).

[c] 'Yes': under illumination (15 W fluorescent lamp); 'no': in the dark.

[d] With respect to the electricity passed (965 C). 'trace': less than 1%; '–': less than the detection limit of GC (< 0.1%); *o*-CT: *o*-chlorotoluene; *p*-CT: *p*-chlorotoluene; BC: benzyl chloride.

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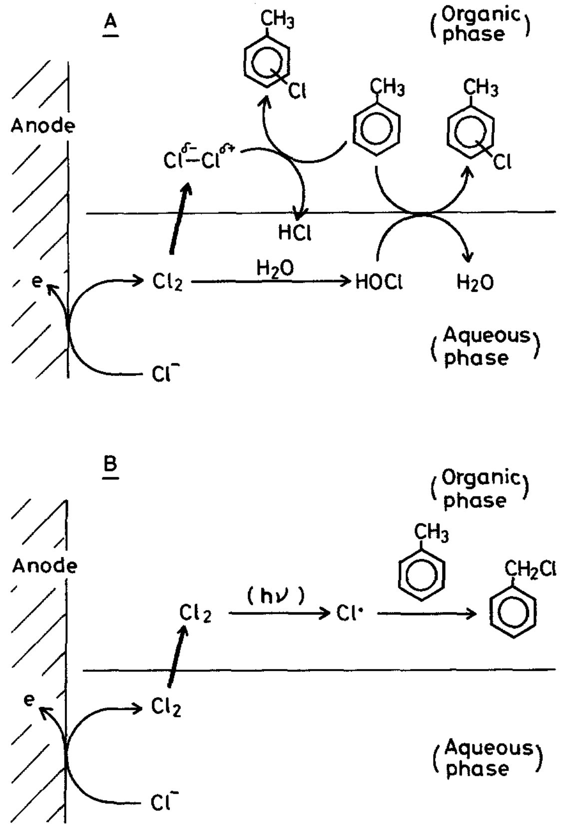

Fig. 1. Reaction schemes for electro-chlorination of toluene by two-phase electrolysis: A, in emulsion system; B, in stationary system.

initiated by the oxidation of chloride ion (Cl^-) in the aqueous phase since the practical oxidation potential of toluene is higher than that of Cl^- [4]. In the emulsion system, the electrochemically formed Cl_2 reacts with the ring carbon of toluene at the interphase between the solvents. The active species which electrophilically reacts with the ring at the 2- or 4-position is either polarized Cl_2 or HOCl. In the stationary system, however, this reaction path is almost negligible because the reaction area of the water/organic interphase is much smaller than that in the emulsion system. The electrochemically evolved Cl_2 is transported to the non-polar organic phase, and then reacts with the methyl group through a radical mechanism which is accelerated by light irradiation. These possible mechanisms are schematically shown in Fig. 1. The photo-assisted process yielding benzyl chloride (Fig. 1B) is similar to the conventional chemical chlorination of aromatic compounds, except for the utilization of electrolytically evolved chlorine *in situ*. In conclusion, it is important to note that the yields and the selectivity of the chlorinated products in the two-phase electrolysis are much affected by the electrolysis conditions. The electrochlorination of other aromatic substrates is also being investigated and the results will be published in the near future.

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