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NOTE

Chlorination of Substituted Aromatics on Graphite Anode

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Electro-chlorination on selected aromatic compounds has been carried out on graphite anode in 1 : 1 water-ethanol solutions. The major anodic products are found to be chloro substituted aromatic compounds. The most probable mechanism for this anodic transformation has been proposed and substantiated by quantitative studies.

Key Words: Chlorination, Substituted aromatics, Graphite anode.

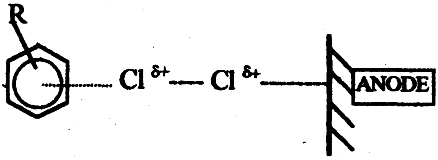
Chlorination of organic compounds is known to have occurred in aqueous acid media[1-3]. Earlier work indicates successful chlorination of benzene in methanol solution in which chlorination was assumed at the anodic surface on adsorbed benzene[4]. Anodic halogenations of the substrate may be expected to proceed either by the conversion of substrate to cationic intermediate followed by its reaction with X^- or by the chemical reaction of electro-generated halogen with the substrate. While recent works explain halogen charge transfer complex at the anode, in the absence of high temperature and irradiation with light. In the present work, electro-chlorination of substituted aromatics like toluene, 1-naphthol, anisole, aniline and nitrobenzene were carried out in aqueous acidic media. Sodium chloride was employed as the electrolyte.

The chemicals were purified by conventional physical methods and were characterized by their physical constants. Rectangular graphite blocks used as electrodes were pretreated and preserved. The electrolyses were carried out in divided H-cell. Polarization studies and preparative electrolyses were performed galvanostatically in aqueous medium containing drops of hydrochloric acid. To ascertain the number of electrons involved, calculative quantities of current were passed through 0.1 M substrate solutions.

After electrolysis, the organic product mixtures were extracted with ether to remove the water-soluble salts and were resolved on TLC plates using benzene-ethyl acetate mixture as eluent. Co-TLC chromatograms were developed with authentic samples as references to distinguish the products. The products were characterized by physical constants and chemical tests. The quantitative product analysis is mainly designed on the basis of comparative intensities of spots developed in the chromatograms.

Current-potential studies on these systems show a negative shift from the background current, indicating the occurrence of electrode process. Preparative electrolyses and chromatographic studies on the product mixtures showed specific products in each case. Electrolyses with methyl methacrylate produced no turbidity. Based on these observations and with reference to earlier electrochemical works on aromatics, two possible mechanisms have been visualized. One in which a chlorine-aromatic charge transfer complex is assumed **(Scheme 1).**

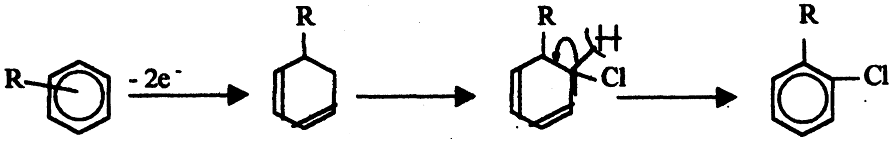
$$\mathrm{NaCl} \longrightarrow \mathrm{Na^+ + Cl^-} \;;\; \mathrm{Cl^-} \xrightarrow{-1e} \mathrm{Cl^{\cdot}} \;;\; 2\,\mathrm{Cl^{\cdot}} \longrightarrow \mathrm{Cl-Cl}$$



Scheme-1

In the present study, the electrolysis was performed at low current density and at laboratory temperature. In earlier works, involving chlorination and bromination of aromatics, it has been established that high current density and high temperature favoured the halogenations by molecular halogen[5]. Further the applied working potential, which is very much lower than the discharge potential of chloride ion to atomic chlorine, is just sufficient for the oxidation of aromatic π-cloud. On the strength of this argument, charge transfer complex mechanism may be ruled out in these processes[6].

Another mechanism in which the overall electro-chlorination involving an initial 2e-oxidation, in the aromatic system leading to the formation of dication I is considered. The attack of chloride ion on the positive centre ultimately results in chloro-substituted aromatic products **(Scheme 2).**



Scheme-2

(II)

The mechanism of *meta* chlorination in nitrobenzene may be explained with an alternative dication **II**, obviously due to the fact that dication **I** is destabilized by the reinforced —I and —M influences of nitro group.

Also from earlier electrochemical reports, it is gathered that radical initiated electrode processes are being favoured by platinum while carbonium ion forming reactions on graphite electrodes[7]. The proposed mechanism can only be established by substantiating the ease of forming the dication intermediate. In this study, this proposition is found to be true by the observation that the total percentage of conversion to the products is higher with electron releasing substituents, *viz.*, hydroxy, methoxy, amino and methyl and is low in the case of electron withdrawing nitro substituents. Among the predominantly electron releasing substituents the following trend in halogenation is observed in acid medium (Table-1).

$$—OCH_3 > —OH > —CH_3 > —NH_2$$

TABLE-1
PRODUCT DISTRIBUTION

Cell: H-Cell
Solvent: 1 : 1 Water-ethanol
[Substrate]: 0.1 M
Supporting Electroyte: 0.1 M Sodium chloride
TLC Adsorbent: Silica gel
Electrodes: Graphite
Current passed: 2F/mol
Temperature: 30 ± 1°C
Eluent: Benzene + 2 drops ethyl acetate

No.	Substrate	Net conversion	Product yield(%)		
			o-Isomer	*p*-Isomer	Others
1.	Toluene	82	52	43	05 (benzyl chloride)
2.	1-Naphthol	86	56	44	00
3.	Anisole	89	16	84	00
4.	Aniline	71	15	32	53 (quinone, etc)
5.	Nitrobenzene	42	00	00	92 (*m*-chloro)

This order is in conformity with the influence of polar effects on dication intermediates, with the exception of the amino function. The probable reason for the exceptional behaviour observed in the case of aniline must have been the possible electron transfer at two different centers, *viz.*, the π cloud of benzene ring[8] and the lone pair on nitrogen[9]. In addition to halogenated anilines, *p*-benzoquinones are also identified.

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