Cathodic Reduction of some Aromatic Compounds in Tetrahydrofuran - water at Mercury Pool

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Cathodic reductions of 1-naphthol, phenol, toluene and phenyl sulphide have been carried out at constant current on preparative scale in 9:1 tetrahydrofuran - water mixture at mercury pool cathode using tetrabutylammonium fluoborate as supporting electrolyte. The products were characterized by UV, IR and ^{1}H NMR and a probable mechanism for the reaction p athway is proposed.

Aromatic and heterocyclic compounds are reduced under diverse reaction conditions like catalytic hydrogenation in presence of heterogeneous and homogeneous catalysis [1], Birch reduction [2], hydrogenation in the presence of phase transfer catalysis [3] etc. Various electrochemical reduction processes have also been developed under variety of reaction conditions: reduction of phenol to cyclohexanol in 2 mol.dm^{-3} sulphuric acid at platinized platinum [4]; use of electrochemically generated solvated electrons for reduction of aromatics [5,6]; cathodic reduction of phenol and 2-naphthol to cyclohexanol and trans-2-decalol respectively in 2 mol.dm^{-3} perchloric acid at platinum foil [7]; electroreduction of some organic compounds in aqueous solutions of tetrabutylammonium salts [8] and electrochemical reduction of pyridine in aqueous solution as a function of pH & electrode material [9] etc. In the present communication, we report the cathodic reduction of some aromatic compounds.

EXPERIMENTAL

1-Naphthol [1], phenol [2], toluene [3], THF (all from SISCO) and phenyl sulphide (4) (from Aldrich) were used without further purification. Tetrabutylammonium fluoborate ($TBA.BF_4$) was prepared by reported method [10].

A two compartment cell consisting of a 250 ml beaker with a porous diaphragm (with provision to hold electrodes, thermometer and magnetic bar) was used for electrolysis. A constant current was passed from a current regulated power supply (fabricated by University Science Instrumentation Centre, University of Rajasthan, Jaipur). The instrument was calibrated before use.

After the completion of electrolysis, the catholyte was filtered and THF was removed by distillation. Water (60 ml) was added to it and the solution was extracted with diethyl ether (3 x 40 ml). The ether layer was washed with dilute HCl (3 x 60 ml) and finally with water (3 x 60 ml). The ether layer, thus obtained was dried over anhydrous sodium sulphate, filtered and the solvent was removed. The residue thus obtained was chromatographed over a column of silica gel and the organic compound was eluted with either petroleum ether (60-80°C) or hexane and ethyl acetate (99:1).

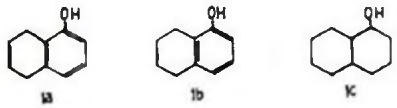
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RESULTS

The preparative scale cathodic reduction of the four aromatic compounds in mixed organic - aqueous solvent (THF-H_2O) was studied at mercury pool cathode (current density 30 mA.cm^{-2}) in order to explore a suitable, simple and convenient electrochemical methodology at reasonably normal reaction conditions. In general, 1g of organic compound was taken in 40 ml of catholyte (THF - H_2O in 9:1 ratio containing 0.25 M TBA BF_4) and reduced at mercury pool cathode. The anode (Pt. foil) was kept in the porous diaphragm containing 15 ml of the anolyte (0.25 M TBA.BF_4 in THF-water in 9:1 ratio). Nitrogen gas was bubbled through the solution and stirring was performed by a magnetic bar. The experimental details of cathodic reduction of the compounds and the products obtained are mentioned in the Table.

Cathodic Reduction of 1-Naphthol

Three compounds 1a, 1b and 1c are identified using m.p., IR and ^{1}H NMR.



Properties of 1a used in identification:

m.p. 73°C, reported 74°C [11]
IR peaks (cm^{-1}): 3520-3390 (b, -OH stretch and aromatic C-H stretch);
1650 (-C=C- stretch);
1540, 1480, 1440 (C=C ring stretch).
^{1}H NMR in CCl_4 with TMS as internal standard (δ in ppm),: 2.2 (s, 4H, - CH_2), 5.1 (s, 1H, -OH), 5.4 (d, 2H, -HC = CH-), 6.4-7.0 (m, 3H, aromatic). 1230(C-O stretching)

Properties of 1b used in identification:

m.p. 69°C, reported 68.5-69°C [12(i)]
IR peaks (cm^{-1}): 3540-3400 (-OH stretch and aromatic C-H stretch); 1560, 1490, 1470 (C=C ring stretch); 1240 (C-O stretch);790, 760 (out of plane C-H bend); 710 (out of plane C=C bend).
^{1}H NMR in CCl_4 (δ in ppm): 1.8-2.0 (s, 8H, - CH_2), 2.6 (d, 2H -CH), 5.0 (s, 1H, -OH), 6.5 (m, 3H, aromatic).

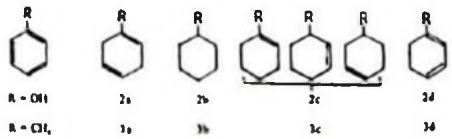
When 1-naphthol was reduced cathodically using current > 10 F / mol, highly reduced product - decahydronaphthol (1c) is obtained.

Properties of 1c used in identification:

m.p. 93°C, reported 93°C [12(ii)]
IR, peaks (cm^{-1}): 3550-3420 (-OH stretching); 2840-2860 (C-H stretching); 1460 (C-H bending); 1075 (C-O stretch).
^{1}H NMR in CCl_4 (δ in ppm): 1.5 (s, 14H, - CH_2), 1.8 (s, 3H -CH), 3.7 (s, 1H, -OH).

Cathodic Reduction of Phenol

In a typical experiment, cathodic reduction of phenol gave cyclohexanol (2b) as major product (47%) alongwith small amount (10%) of 1-hydroxy-1, 4-cyclohexadiene (2a) and a mixture of hydroxycyclohexenes (2c) The separation of 2a and 2b is achieved by column chromatography on silica gel by eluting from hexane and ethyl acetate (99:1). 2c could not be separated and the combined yield of isomeric hydroxycyclohexenes was reported (5%).



Properties of 2a used in identification:
IR peaks (cm^{-1}): 3380-3320 (-OH stretch) 2930 (s) (C-H stretch); 1680(s) 1640(s) (C=C ring stretch); 1340 (C-H bend); 1240 (C-O stretch).
^1H NMR in $CDCl_3$ (δ in ppm): 2.1-2.6 (m, -4H, $-CH_2$), 3.8 (s, 1H -OH), 4.3 (t, 1H,), 5.65 (s, 2H,olefinic).

Properties of 2b used in identification:
b.p. 160-161°C, reported 161°C [12(iii)]
IR peaks (cm^{-1}): 3460-3310 (-OH stretch); 2810 (s) (C-H stretch); 1420 (C-H bend); 1073 (C-O stretch).
^1H NMR in $CDCl_3$ (δ in ppm): 1.15-2.95 (m, 10H, $-CH_2$),3.85 (s, 1H, -CH), 5.45 (S, 1H, -OH).

Cathodic Reduction of Toluene

In a typical experiment cathodic reduction of toluene yielded 3a (12%), 3b(52%) and isomeric methyl cyclohexenes (3c) (5%). The products were separated over silica gel by eluting with hexane-ethyl acetate (99:1) solvent system.

Properties of 3a used in identification:
IR peaks (cm^{-1}): 2910, 2860, 2720 (C-H stretch); 1690, 1660 (C=C stretch); 1410, 1350, 1220 (C-H bend).

Table 1

Cathodic reduction of some organic compounds at mercury pool cathode

Electrolyte 0.25 M $TBA.BF_4$ in THF-H_2O (9:1); Temperature of the cell 20°C.
Reduction potentials are measured with reference to SCE ; current density 30 $mA.cm^{-2}$;

Compound Reduced	Charge $F.mol^{-1}$	Red. Potl (V) initial , final	Product & (% Yield*)
1 naphthol	4	-2.70 , -2.90	1a (9), 1b (34)
	10	-2.70 , -3.00	1a (6), 1b (14), 1c (26)
	12	-2.70 , -3.10	1a (~4), 1b (9), 1c (45)
	15	-2.70 , -3.20	1b (~5), 1c (60)
	20	-2.70 , -3.38	1b (~3), 1c (70)
phenol	6	-2.80 , -3.05	2a (10), 2b (47)
	10	-2.80 , -3.18	2a (4), 2b (64)
toluene	6	-2.75 , -3.15	3a (12), 3b (52)
	10	-2.75 , -3.30	3a (6), 3b (63)
phenyl sulphide	4	-2.85 , -3.18	4a (20), 4b (57)
	5	-2.85 , -3.25	4a (22), 4b (64)

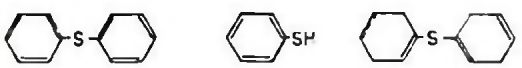
* The balance is starting material

^1H NMR in $CDCl_3$ (δ in ppm): 1.7 (s, 3H, CH_3), 2.75 (m, 4H $-CH_2$), 4.45 (t, 1H), 5.6 (s, 2H).
UV (methanol) λ_{max} = 223 (log ε = 3.48)

Properties of 3b used in identification:
b.p. 99-100°C, reported 100°C [12(iv)]
IR peaks (cm^{-1}): 2890, 2740 (C-H stretch); 1440, 1370, 1230 (C-H bend).
^1H NMR (δ in ppm) : 1.0 (s, 3H, CH_3), 1.1-2.15 (m, 11H $-CH_2$ & -CH)

Cathodic Reduction of Phenyl sulphide

After the completion of the electrolysis and the work up, the products obtained were chromatographed on silica gel by hexane and ethyl acetate (99:1). 4a and 4b are obtained in 20% and 57% in a typical experiment.



4 4a 4b

Properties of 4a used in identification:
4a was charactrized by comparing IR and NMR spectra with the authentic sample of thiophenol.

Properties of 4b used in identification:
IR peaks (cm^{-1}): 2895-2730 (-CH stretch); 1700, 1660 (C=C stretch); 1460, 1380, 1240 (C-H bend); 690 (C-S stretch).
^1H NMR in CCl_3 (δ in ppm): 2.84 (m, -8H, $-CH_2$), 5.10 (m, 2H), 5.75 (d, 4H).
UV (methanol) :λ_{max} 221 (log ε = 3.90)

DISCUSSION

The survey of the pertinent literature reveals that 1-naphthol gives 1a under a variety of reaction conditions eg. sodium-t-amylalcohol-ammonia [11], potassium-ethanol-ammonia [13] and in lithium-ethanol-ammonia [14]. Lithium-methylamine reduction [15] results 1b as main product. Interestingly, the cathodic reduction in the present case at mercury pool cathode in 0.25 M $TBA.BF_4$ solution of THF-H_2O (9:1) gives 1a, 1b and 1c. The ratio of 1a, 1b and 1c is mainly dependent upon the charge transfered (see table). 4F.mol^{-1} yielded 1a and 1b in 9% and 34% respectivley, but 10F.mol^{-1} gave 6%, 14% and 26% of 1a, 1b and 1c respectively. With further increase of charge transfered, the amount of 1c increases at the expense of other products *viz.*, 1a and 1b. At 20 F.mol^{-1}, 1c is the major product (70%) alongwith minor quantity of 1b (~3%).

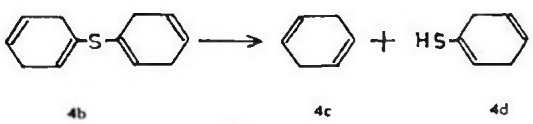
Cathodic reduction of phenol and toluene at 6 F.mol^{-1} gave 2a and 3a as minor product (4% and 12% respectively), while highly reduced product *viz.*, 2b and 3b are obtained as main product 47% and 52% respectively. Charge equivalent to 10 F.mol^{-1} yielded 2b and 3b in good amount 64% and 63% respectively.

It is to mention that the formation of 1-substituted 1,3-cyclohexadiene *viz.*, 2d and 3d are also expected. But these structures were not indicated on the basis of ^1H NMR spectral studies. The VU spectral studies of 3a gave λ_{max} (methanol) 223nm (logε = 3.48).

The low λ_{max} value for 3a suggest that the cyclohexadiene derivative must be a non-conjugated system. These observation are in agreement with the earlier report [16], wherein the λ_{max} for 1-methoxy 1,3-cyclohexadiene, conjugated system, was reported at 274 nm (ε_{max} 424). Further, the NMR data published for 1-methoxy-1, 4-cyclohexadiene are matching with 2a and 3a in a closer range. Isomeric 2c and 3c are also obtained as minor product in the

cathodic reduction. Efforts to separate these isomers were unsuccessful and therefore a combined yield was reported.

Cathodic reduction of phenyl sulphide gave 4a and 4b. Their yields and experimental details are summarized in the Table. 4a was characterized by comparison with IR and NMR spectra of authentic sample of thiophenol. The ^1H NMR spectra for 4b shows 3.3' and 4.4' olefinic protons at δ = 5.75 and 2.2' and 5.5' methylene protons at δ = 2.84. These data are in agreement with the earlier observations [16] and with the data of 1,4 cyclohexadine derivatives viz., 2a and 3a. The UV data of 4b shows λ_{max} (methanol) at 221 nm (logε = 3.90) supporting that 4b should have non-conjugated system of double bonds. The cathodic reduction of 4b corresponding to 20F.mol^{-1} results 1,4 -cyclohexadiene (4c) and 1,4 - dihydrothiophenol (4d) in equal yield.



4b 4c 4d

The ratio was determined by comparison of integrals of olefinic protons of 4c and 4d. While the reaction mechanism of cathodic reduction at mercury pool in the presence of tetrabutyl ammonium ion is a subject of further systematic studies, we propose the possibility of following mechanism involving tetrabutyl ammonium amalgams:

$$TBA^{\cdot} + e + n\ Hg \longrightarrow TBA(Hg)_n$$

$$TBA(Hg)_n + Ar \longrightarrow Ar^{-} + TBA^{\cdot} + n\ Hg$$

The radical ion generated may undergo the following sequence of the reaction.

$$Ar^{-} + H^{\cdot} \longrightarrow ArH^{\cdot}$$

$$ArH^{\cdot} + TBA(Hg)_n \longrightarrow ArH^{-} + TBA^{\cdot} + n\ Hg$$

$$ArH^{-} + H^{\cdot} \longrightarrow ArH_2 \text{ etc.}$$

REFEREENCES

1. Smith in Augustine, *Reduction Techniques and Applications in Organic Synthesis*, **Marcell Dekker, New York**, (1968) pp.309-395; Weitkamp, *Advt. Catal.* **18** (1968) 1-110 (for naphthalene); Freifelder, *Advt. Catal.* **14** (1963) 203-253 (for pyridines and quinolenes).
2. A.J. Birch and G.S.R. Subba Rao, *Adv. Org. Chem.*, **8** (1972) pp 1-65; E.M. Kaiser, *Syntheses* **391** (1972); R.G. Harvey, *Synthesis* **161** (1970); Huckel, *Fortschr Chem. Forsch.* **6** (1966) 197.
3. Januszkiewicz and Alper, *Organometallics* **2** (1983) 1055.
4. F. Fichter and R. Stocker, *Ber.*, **47** (1914) 2003.
5. H.W. Sternberg, R.E. Markby, I. Wender and D.M. Mohilner, *J.Electrochem. Soc.* **113** (1966) 1060; , *J.Am.Chem.Soc.*, **89** (1967) 186 & **91** (1969) 4191.
6. Ram A. Mishra and Ashok K Yadav, *Bull. Chem. Soc. Japan*, **55** (1982) 347.
7. R.A. Mishra and B.K. Sharma, *Electrochim Acta*, **24** (1979) 727.
8. E.K. Miller, K.E. Swenson, D. Zemach, *J.Org. Chem.* **48** (1983) 4210; R.I. Pacut and E.K. Miller, *J.Org. Chem.*, **51** (1986) 3468 E.K. Miller and R.I. Pacut, *Tetrahedron*, **42** (1986) 2185.
9. Yu.D. Smirnov, E.N. Shitoba, G.F. Shaidulina, A.P. Tomilov, V.F. Pavlichenko, *Electrokhimiya* **28(7)**, (1992) 1073.
10. H.O. House, E. Feng, N.P. Peet, *J.Org. Chem.*, **36** (1971) 2371.
11. A.J. Birch, *J.Chem. Soc.*, **(1944)** 430
12. I. Heilbron and H.M. Bunbury, in *Dictionary of Organic Compounds*, **Eyre and Spottis Woode** (1953) (i) Vol.4, pp 439; (ii) vol 2 p3 (iii) Vol. 1,P.637 (iv) Vol.4, p.514.
13. J.F. Eastham, D.R. Larkin, *J.Am.Chem.Soc.*, **80** (1958) 2887.
14. C.D. Guthsche, H.H. Peter, *Organic Synthesis coll. Vol.IV*, **(1963)** 887.
15. R.A. Benkeser, R.F. Lambert, P.W. Ryan, D.G. Stophy, *J.Am.Chem.Soc.* **80** (1958) 6573.
16. A.J. Birch, G.S.R., Subba Rao, *Aust. J.Chem.*, **23** (1970) 1641.