

Synthesis of Phenol from Benzene by Electroreduction of Oxygen in $\text{CF}_3\text{SO}_3\text{H}$

Ryuichiro Ohnishi* and Akiko Aramata

Research Institute for Catalysis, Hokkaido University, Sapporo 060, Japan

A one-step synthesis of phenol from benzene was achieved at a current efficiency of 22–41, 11, and 6% on graphite, Au black, and Pt black cathodes, respectively, by electrochemical reduction of oxygen gas in a highly acidic solvent, $\text{CF}_3\text{SO}_3\text{H}$, at room temperature.

Direct synthesis of phenols from aromatic compounds poses problems owing to side reactions such as further oxidation of phenol and dimerization or polymerization.¹ However, phenol was obtained in 80 and 16% yields respectively† from benzene and 90% H_2O_2 in the highly acidic solvents $\text{FSO}_3\text{H}-\text{SbF}_5$ (1 : 1)– SO_2ClF ($H_0 = -25$) and $\text{FSO}_3\text{H}-\text{SO}_2\text{ClF}$ ($H_0 = -15.1$)^{2,3} at solid CO_2 temperature.⁴ Protonation of H_2O_2 and phenol to H_3O_2^+ and PhOH_2^+ respectively, is responsible for such high yields since H_3O_2^+ is a very active electrophile⁵ and PhOH_2^+ is unreactive to electrophilic attack.⁶

It has been reported that H_2O_2 can be obtained in high yields by electrochemically reducing oxygen gas on Hg, Au,

and graphite but in low yield on Pt.⁷ This communication reports a new method for the direct synthesis of phenol by electrochemical reduction of oxygen and subsequent chemical oxidation of benzene in a highly acidic medium, trifluoromethanesulphonic acid (TFA, $H_0 = -14.4$).²

A TFA solution containing H_2O or Me_4NCl was introduced into an electrolytic cell with three compartments for cathode, anode, and reference electrode, respectively. Cathodes employed were a graphite rod of spectroscopic grade from Union Carbide, Au black, and Pt black. Oxygen gas bubbled through benzene was supplied to the cathode compartment. The solution in the cathode compartment (*ca.* 3 ml) was

Table 1. Phenol obtained from benzene by O_2 electroreduction on various electrodes and solutions at room temperature.

Electrode	Potential/V vs. R.H.E. ^a	Time/h	Charge passed/C	Yield of phenol/ $\times 10^{-6}$ mol	Current efficiency ^f of phenol/%
Graphite ^b	0	24	3.67	6.84	36
Graphite ^b	-0.2	9	5.24	7.33	27
Graphite ^b	-0.2	7.4	2.73	3.11	22
Graphite ^b	-0.5	7.5	8.8	12.8	28
Graphite ^b	-0.5	5.0	6.95	10.8	30
Graphite ^c	-0.4	9.1	4.41	9.37	41
Graphite ^d	-0.4	8.0	5.63	9.33	32
Graphite ^e	-0.2	5.5	7.64	0	0
Au black ^b	-0.2	7.7	9.67	5.51	11
Pt black ^b	0	5.5	5.94	1.94	6.3

^a R.H.E. = reversible hydrogen electrode. ^b 0.63 M H_2O TFA solution. ^c 0.1 M Me_4NCl TFA solution. ^d 0.31 M H_2O TFA solution. ^e 0.5 M H_2SO_4 aqueous solution. ^f For a definition see footnote†.

analysed for phenol by g.l.c. after a certain period of electrolysis at room temperature. A blank experiment left standing for 24 h with no electrolysis taking place using graphite in a 0.63 M H₂O-TFA solution gave 2.5×10^{-7} mol of phenol, which is close to the detection limit of g.l.c.

The results of potentiostatic electrolysis under varying conditions are shown in Table 1. On graphite in 0.63 M H₂O, the current efficiency† was 22–36%. Changing the applied potential did not change the efficiency although at the more negative potentials obviously the current was larger. An increase in the efficiency was noted in the case of 0.1 M Me₄NCl but not in the case of 0.31 M H₂O although both solutions are expected to be more acidic than that containing 0.63 M H₂O. In less acidic 0.5 M H₂SO₄ aqueous solution no trace of phenol could be detected at the graphite cathode. The efficiency on Au black and Pt black in 0.63 M H₂O was 11 and 6.3%, respectively, which was lower than on graphite.

Constant current (0.5 mA) electrolysis of 1.1×10^{-4} mol of benzene on graphite in 0.63 M H₂O was carried out for 14 h to give 1.2×10^{-5} mol phenol in 11% yield,† which is

† Yield and current efficiency are $100 \times (\text{moles of phenol})/(\text{moles of benzene})$ and $100 \times (\text{moles of phenol})/(\text{charge passed})/(2 \times F)$, respectively, where F is the Faraday constant. The latter equation is based on the assumption that two electrons are necessary for the formation of one molecule of H₂O₂ (phenol) from one of O₂.

comparable to the 16% for benzene-H₂O₂ (1:1)-FSO₃H system at solid CO₂ temperature.⁴

Received, 18th April 1986; Com. 514

References

- 1 J. Wellman and E. Steckhan, *Chem. Ber.*, 1977, **110**, 3561; A. Aramata, *J. Electroanal. Chem.*, 1985, **182**, 197; (b) K. Nyberg, 'Encyclopedia of Electrochemistry of the Elements,' eds. A. J. Bard and H. Lund, Marcel Dekker, New York, 1978, vol. 11, p. 3; (c) O. Hammerich and V. D. Parker, *Adv. Phys. Org. Chem.*, 1984, **20**, 55; G. Brilmyer and R. Jasinski, *J. Electrochem.*, 1982, **129**, 1950.
- 2 G. A. Olah, G. K. S. Prakash, and J. Sommer, 'Superacids,' Wiley, New York, 1985, p. 35.
- 3 *H*₀ denotes the degree of acidity. See C. H. Rochester, 'Acidity Functions,' Academic Press, London, 1970, p. 1.
- 4 G. A. Olah and R. Ohnishi, *J. Org. Chem.*, 1978, **43**, 865.
- 5 R. W. Alder and M. C. Whiting, *J. Chem. Soc.*, 1964, 4707.
- 6 G. A. Olah and Y. K. Mo, *J. Org. Chem.*, 1973, **38**, 353.
- 7 M. R. Terasevich, A. Sadkowski, and E. Yeager, 'Comprehensive Treatise of Electrochemistry,' eds. B. E. Conway, J. O'M. Bockris, E. Yeager, S. U. M. Khan, and R. E. White, Plenum Press, New York, 1983, vol. 7, p. 301; D. J. Schriffirin, 'Electrochemistry (Specialist Periodical Report),' ed. D. Pletcher, The Royal Society of Chemistry, London, 1983, vol. 6, p. 126; J. P. Randin, ref. 1(b) 1976; vol. 7, p. 2; J. P. Hoare, *Adv. Electrochem. Electrochem. Engineering*, 1967, **6**, 201.