Tetrahedron Vol. 47, No. 4/5, pp. 841-850, 1991
Printed in Great Britain

0040-4020/91 $3.00+.00

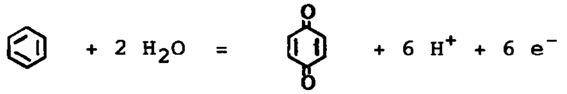
DUET ELECTROSYNTHESIS OF p-BENZOQUINONE FROM BENZENE

Sotaro Ito,* Mikio Iwata, and Kazuo Sasaki
Department of Applied Chemistry, Faculty of Engineering,
Hiroshima University, Saijo, Higashi Hiroshima 724 Japan

(*Received in USA* 15 *August* 1990)

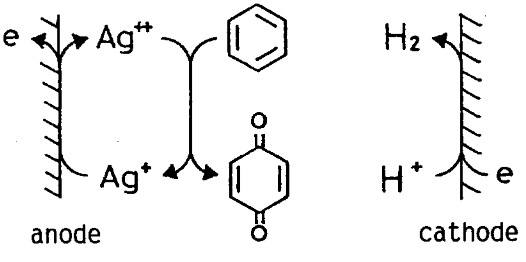
ABSTRACT: The combination of anodic oxidation of benzene using Ag(I)/Ag(II) mediator with cathodic oxidation of benzene using Cu(I)/Cu(II) mediator in a single electrolytic cell produces p-benzoquinone selectively in both anodic and cathodic chambers.

In an electrolytic reaction, the theoretical yield of a product per unit electric charge is univocally determined by the number of electrons(n) required to convert one molecule of the reactant to the final product. For example, the anodic oxidation of benzene to p-benzoquinone (BQ) is, as seen in eq.(1), a six-electron reaction

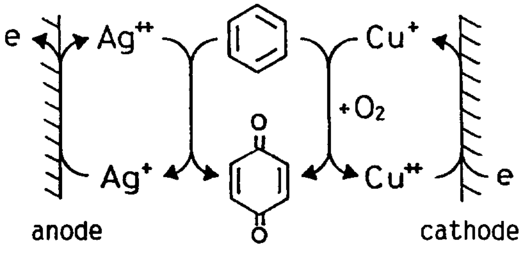


(1)

and the theoretical Faradaic yield of BQ expressed by mmol per one Faraday of electric charge is 1000/6 = 166.7 mmol F^{-1}. In practice, the Faradaic yields of BQ hitherto reported are 103 mmol F^{-1} in the oxidation of benzene on PbO_2 anode[1] and 92 mmol F^{-1} in the indirect oxidation using Ag(I)/Ag(II) mediator.[2] These Faradaic yields of BQ amount to 62 and 55% of the theoretical yield, respectively. Since the direct production of BQ from benzene is one of the targets in industrial chemistry, much efforts to optimize the electrolytic conditions and to improve the Faradaic yield of BQ up to near the theoretical have been done but in vain. Furthermore, no details of the side reaction(s), accompanying reaction (1) and decreasing the yield of BQ, have been elucidated yet.



Scheme 1 Conventional anodic oxidation.



Scheme 2 Duet electrosynthesis.

The purpose of this work is to establish a novel principle for improving the Faradaic yield of BQ in the electrolysis of benzene. The strategy for accomplishing this purpose is effective utilization of the reaction(s) at the counter electrode. In the usual anodic oxidation of benzene, cathodic current is wastefully consumed to reduce hydrogen ions to hydrogen gas, as shown in Scheme 1. If benzene can be oxidized in the cathode chamber as well as in the anode chamber, the Faradaic yield of BQ is expected to increase markedly, presumably by two times. In the previous studies, we have demonstrated that benzene is oxidized to give hydroquinone (HQ) and phenol in the cathode chamber in the presence of both molecular oxygen as an oxidant and Cu(I)/Cu(II) redox couple as a mediator.[3,4] The actual oxidant in the cathode chamber is hydroxyl radicals, which are formed according to reactions (2) and (3).[5]

$$2\ \mathrm{Cu(I)} + \mathrm{O_2} + 2\ \mathrm{H^+} = 2\ \mathrm{Cu(II)} + \mathrm{H_2O_2} \tag{2}$$

$$\mathrm{Cu(I)} + \mathrm{H_2O_2} + \mathrm{H^+} = \mathrm{Cu(II)} + \cdot\mathrm{OH} + \mathrm{H_2O} \tag{3}$$

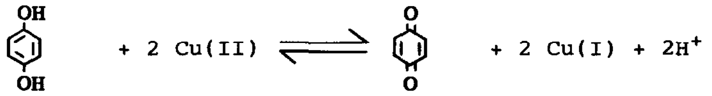
The combination of the "cathodic oxidation of benzene" with the usual anodic oxidation of benzene should constitute an effective electrosynthetic system.

In the present paper, we would like to describe a novel electrolytic system, which we named Duet Electrosynthesis. The proposed electrolytic system can convert benzene to BQ selectively, as illustrated in Scheme 2, in both anode and cathode chambers of a single electrolytic cell. The anodic reaction used is indirect oxidation of benzene by use of Ag(I)/Ag(II) redox mediator, because of its high Faradaic yield.

Results and Discussion

1. Cathodic Oxidation of Benzene using Cu(I)/Cu(II) Redox Couple.

Benzene can be oxidized with molecular oxygen in the cathode chamber, where Cu(II) ions are reduced on the electrode to give Cu(I) ions.[4] The main products at pH 3.5 is hydroquinone with Faradaic yield of 94 mmol F^{-1} under the optimum conditions, while the molar ratio of BQ (the oxidized form of HQ) to HQ increases with increasing pH, according to the equilibrium reaction (4)



(4)

The equilibrium (4) should be shifted to the right side by removing i) BQ with solvent extraction, ii) Cu(I) ions by oxidation with O_2, and iii) H^+

ions by neutralization. The continuous solvent extraction of BQ is expected, therefore, to produce BQ selectively in the cathode chamber. Prior to the electrolytic oxidation, some experiments concerning the conversion of HQ to BQ were done. Result in Figure 1 shows the effective oxidation of HQ to BQ with Cu(II) ions by use of continuous extraction with different amount of benzene under O_2 atmosphere. The addition of more than 12 ml of benzene into the 100 ml of the catholyte almost quantitatively converted HQ to BQ. The result in Figure 2 was peculiar at first glance in that the yield of BQ (ca. 0.68 mmol) exceeds the initial amount of HQ added (0.50 mmol). Taking into account the presence of benzene, Cu(I) ions and O_2 in the system, however, it is evident that the increment of BQ is derived from the oxidation of benzene, not of HQ. Thus the continuous extraction of BQ with benzene brings about additional advantage.

The electrolytic oxygenation of benzene in the cathode chamber with the continuous extraction of BQ, carried out in the apparatus shown in Figure 3, produced BQ selectively in Faradaic yield of 128-148 mmol F^{-1} at pH 4.6 under controlled cathode-potential conditions. Only a small amount of HQ (5 mmol F^{-1}) and phenol (30 mmol F^{-1}) accompanied BQ, while an appreciable amount of HQ (40-80 mmol F^{-1}) was formed in the oxidation without the solvent extraction. It is noteworthy that the Faradaic yield of BQ in the cathodic oxidation with the solvent extraction corresponds to 75-89% of the theoretical yield of BQ in the anodic oxidation of benzene.

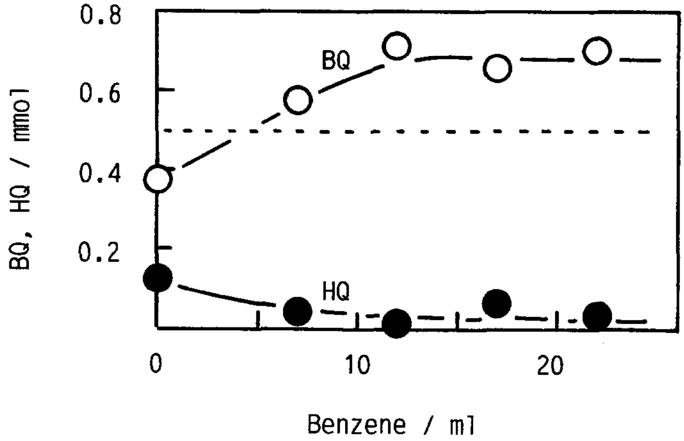


Figure 1 Oxidation of hydroquinone with Cu(II) ions promoted by continuous extraction of benzoquinone.

HQ: 0.5 mmol, Cu(II): 0.2 mmol, atmosphere: O_2,
pH: 4.6, reaction time: 1 h.

2. Anodic Oxidation of Benzene using Ag(I)/Ag(II) Redox Couple.

Anodic conversion of benzene to BQ can be done by indirect oxidation by use of a mediator, which oxidizes benzene in high valence state to give low valence species and is reoxidized in low valence state to regenerate high valence species. Ag(I)/Ag(II) redox couple works as a mediator for the oxidation of benzene, though the Faradaic yield is 92 mmol F^{-1} (55% of the theoretical yield) even under the optimum electrolytic conditions.[2] Accordingly, several metal sulfates are tested as a redox mediator for the indirect oxidation of benzene. Among the seven metal sulfates, silver(I) sulfate was confirmed to be effective for the production of BQ, as summarized in Table 1. The sulfates of Co(II), Fe(III) and Cu(II) showed no effect as a mediator as seen in the yield of BQ and observed anode potential, while Mn(II), Ce(IV) and Ce(III) sulfates played a negative role. Since the Faradaic yield of BQ obtained in the Ag(I)/Ag(II) system , 112 mmol F^{-1}, exceeds the maximum value hitherto reported (92 mmol F^{-1}),[2] further experiments for searching the optimum electrolytic conditions have been done, as described in the following.

At first, the effect of the counter ions of the silver salts on the Faradaic yield of BQ was examined and shown in Table 2. The anolytes were 2 M solution of the corresponding acid. Among the five silver(I) salts, the perchlorate gave the highest Faradaic yield, 140 mmol F^{-1}, which amounts to 84% of the theoretical yield. The tetrafluoroborate, sulfate and nitrate of silver(I) also produced BQ in moderate yield, while the acetate gave only a small amount of BQ probably because of the oxidation of acetate ions

Table 1. Anodic oxidation of benzene in the presence of metal ions.[a)]

Metal sulfate	Faradaic yield of BQ (mmol F^{-1})	Observed potential of anode (V vs Hg/Hg_2SO_4 electrode)
None	32	1.36
$MnSO_4$	0	0.82
$Ce_2(SO_4)_2$	3	0.97
Ag_2SO_4	112	1.18
$CoSO_4$	32	1.36
$Fe_2(SO_4)_3$	29	1.36
$CuSO_4$	28	1.36
$Ce(SO_4)_2$	12	1.40

a) Controlled-current electrolysis (1.3 mA cm^{-2}), metal ion: 50 mM, benzene: 3 ml, anolyte: 100 ml of 1 M H_2SO_4.

with either Ag(II) or Ag(III) species. Accordingly, silver(I) perchlorate was exclusively used in the following experiments.

The Faradaic yield of BQ in the Ag(I)/Ag(II) system slightly depends on the initial concentration of silver (I) perchlorate, though the yield of BQ was essentially constant above 50 mM of Ag(I) ions as seen in Table 3. The yield of BQ also depends on the concentration of perchloric acid. The

Table 2. Indirect oxidation of benzene using various silver(I) salts.[a)]

Ag(I) salt	Acid	Faradaic yield of BQ[b)] (mmol F^{-1})
$AgClO_4$	$HClO_4$	142 (85%)
$AgBF_4$	HBF_4	118 (71%)
Ag_2SO_4	H_2SO_4	110 (66%)
$AgNO_3$	HNO_3	78 (47%)
CH_3COOAg	CH_3COOH	10 (6%)

a) Controlled anode-potential electrolysis at 1.18 V vs Hg/Hg_2SO_4 electrode, Ag(I) ion: 50 mM, H^+: 2 M, benzene: 3 ml.

b) Values in parenthesis are percentage to the theoretical yield.

Table 3. Effect of concentration of the silver(I) perchlorate.[a)]

$AgClO_4$ (mM)	Faradaic yield of BQ[b)] (mmol F^{-1})	Observed potential of anode (V vs Hg/Hg_2SO_4 electrode)
1	105 (65%)	1.28
5	114 (68%)	1.25
25	124 (74%)	1.20
50	140 (85%)	1.18
100	140 (85%)	1.11
500	144 (87%)	1.13

a) Controlled-current electrolysis at 1.3 mA cm^{-2}, $HClO_4$: 2 M, benzene: 3 ml.

b) Values in parenthesis are percentage to the theoretical yield.

maximum yield (138-144 mmol F^{-1}) was obtained in 2-4 M of perchloric acid as shown in Table 4.

The observed higher yield of BQ (85% of the theoretical yield for the anodic oxidation of benzene) in the Ag(I)/Ag(II) system than that in the direct oxidation on PbO_2 anode (62% yield) indicates that some mechanism to minimize side reactions (such as formation of o-quinone) are operating in the Ag(I)/Ag(II) system. The selective formation of BQ suggests that the active species introducing the second oxygen atom into benzene nucleus is a bulky AgO^+ species, which is generated by the disproportionation of Ag(II) to Ag(I) and Ag(III) followed by reaction (6)[6-7]

$$2\ Ag(II) = Ag(I) + Ag(III) \qquad (5)$$

$$Ag(III) + H_2O = AgO^+ + 2\ H^+ \qquad (6)$$

As does CuO_2^+ in the selective formation of HQ in the Cu(I)/Cu(II) system,[8] AgO^+ should favor the selective formation of BQ with a steric effect.

For the production of BQ in commercial scale, not only the Faradaic yield of BQ but also the rate of the reaction are important factors. As shown in Table 5, the effect of current density (mA cm^{-2}), which is a measure of the reaction rate per unit surface area of the electrode, on the yield of BQ is apparently remarkable: The yield increases with decreasing the current density to reach a maximum (85%) below the current density of 1.3 mA cm^{-2}. Since the observed potentials of the anode also vary with the

Table 4. Effect of concentration of perchloric acid.[a)]

$HClO_4$ (M)	Faradaic yield of BQ[b)] (mmol F^{-1})	Observed potential of anode (V vs Hg/Hg_2SO_4 electrode)
0.1	40 (24%)	1.27
0.5	63 (38%)	1.24
1	113 (68%)	1.21
2	140 (84%)	1.18
3	138 (83%)	1.18
4	144 (86%)	1.17
6	43 (26%)	1.28

a) Controlled-current electrolysis at 1.3 mA cm^{-2}, $AgClO_4$: 50 mM, benzene: 3 ml.

b) Values in parenthesis are percentage to the theoretical yield.

Table 5 Effect of current density on yield of benzoquinone.[a)]

Current density ($mA\ cm^{-2}$)	Faradaic yield of BQ[b)] ($mmol\ F^{-1}$)	Observed potential of anode (V vs Hg/Hg_2SO_4 electrode)
0.36	140 (85%)	1.17
1.3	140 (85%)	1.18
1.8	133 (80%)	1.20
3.6	121 (73%)	1.21
7.1	112 (67%)	1.23
11	72 (43%)	1.25
18	46 (28%)	1.32
25	36 (22%)	1.35
36	38 (23%)	1.41

a) Controlled-current electrolysis at 10-1000 mA on Pt plate of 28 cm^2 surface area, $AgClO_4$: 50 mM, $HClO_4$: 2 M, benzene: 3 ml.

b) Values in parenthesis are percentage to the theoretical yield.

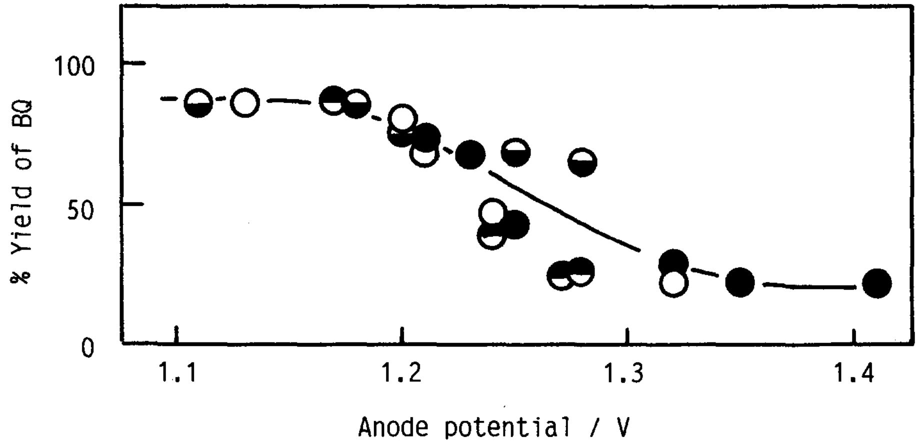


Figure 2. Effect of anode-potential on yield of benzoquinone.

○ : Controlled anode-potential electrolysis at 50 mM of $AgClO_4$ and 2 M of $HClO_4$,

◒ : from Table 3 (under controlled current at 1.3 mA cm^{-2}),

◓ : from Table 4 (under controlled current at 1.3 mA cm^{-2}),

● : from Table 5 (under controlled current at 0.36-3.6 mA cm^{-2}).

current density as seen in Table 5, one must determine whether the Faradaic yield of BQ is controlled by the current density or by the potential of the anode. The effect of the anode potential on the yield of BQ can be directly observed in the electrolysis under the controlled anode-potential conditions and shown in Figure 2. From the results in Figure 2 and Tables 3, 4 and 5, it is apparent that the anode potential is the key factor for controlling the Faradaic yield of BQ: the low yield of BQ was observed when the anode potential deviates far from 1.18 V, even at 1.3 mA cm^{-2}. Evolution of O_2 gas on the anode became marked with increasing the anode potential and decreasing the yield of BQ. Accordingly, one can conclude that the oxidation of water to O_2 competes with the oxidation of Ag(I) ions on the anode at higher anode potential.

3. Duet electrosynthesis of benzoquinone.

The combination of these cathodic and anodic reactions in a single cell has realized an efficient electrolytic system. As demonstrated in Table 6, BQ was selectively formed from benzene in both cathodic and anodic chambers by use of the continuous extraction cell (Figure 3) in the Faradaic yield of 270 mmol F^{-1}, which is essentially identical with the sum of the yield of BQ obtained in the separate cathodic and anodic oxidation of benzene. The observed anode-potential in the Duet electrolysis at 20 mM of silver(I) perchlorate under controlled cathode-potential lies in the range 1.19-1.15 V, which is the optimum anode-potential as in Figure 2. An appreciable amount of HQ was accompanied in the Duet electrolysis without the solvent extraction.

Table 6. Duet electrosynthesis of benzoquinone from benzene.$^{a)}$

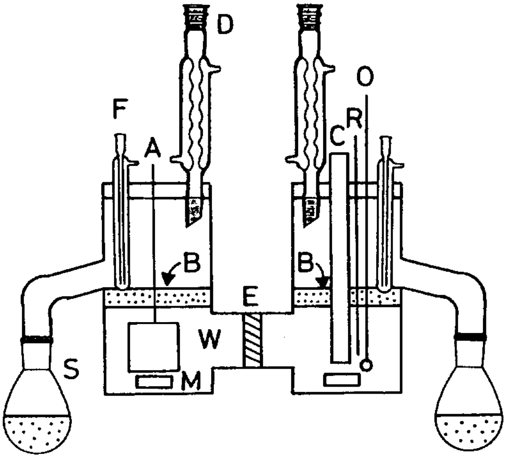
$AgClO_4$ (mM)	$CuSO_4$ (mM)	Continuous extraction	Faradaic yield (mmol F^{-1})				
			Anode	Cathode			Total
			BQ	BQ	HQ	PhOH	BQ
5	5	without	96	24	75	12	120
5	5	with	122	148	5	31	270
20	20	without	126	64	39	15	190
20	20	with	141	128	6	29	269

a) Controlled cathode-potential conditions at -0.5 V vs Hg/Hg_2SO_4 electrode, electric charge: 10 mF.

Experimental

Materials and Analysis. All the chemicals were the highest grade commercial materials which were used without further purification. Oxidation products were analyzed with a JASCO Intelligent HPLC Pump (880-PU) and a JASCO Intelligent UV/VIS Detector (875-UV) coupled with a Shimadzu Chromatopac C-R6A. The separation column was a Cica-MERCK Hibar Lichrosorb RP-18 (5 μm) and the eluent was a mixture of acetonitrile (14%) and a phosphate buffer (86%, pH 3.5).

Electrolysis of benzene. An electrolytic apparatus illustrated in Figure 3 was used. A standard procedure is as follows. Into a H-shaped glass cell (5 cm diam and 9 cm high) divided by a cation-exchange membrane (Tokuyama Soda Neosepta CM-1 or C66-10F) were added 100 ml of an anolyte (0.2 M perchloric acid containing 50 mM of silver(I) perchlorate) and 100 ml of a catholyte (0.2 M acetate buffer of pH 4.6 containing 5 mM of copper(II) sulfate, 50 mM of sodium sulfate and 5 ml of acetonitrile). The electrode material was a carbon rod of 13 mm diam (15 cm^2) as cathode and a Pt plate (28 cm^2) as anode. In the cathodic oxidation of benzene, 3 ml of benzene was added into the catholyte and copper(II) sulfate was electrolyzed at 25 ± 5°C, with bubbling of O_2 (10 ml min^{-1}) and vigorous stirring (1100 rpm), under controlled potential conditions (-0.5 V vs Hg/Hg_2SO_4 electrode) with aid of a potentiostat (Hokuto Denko HA-301) and a digital coulometer (Hokuto Denko HF-201). In the anodic oxidation, 3 ml of benzene was placed into the anode chamber and silver(I) perchlorate was electrolyzed



A: anode (Pt plate)
B: benzene layer
C: cathode (carbon rod)
D: reflux condenser
E: cation exchange membrane
F: condenser
M: stirring bar
O: inlet of oxygen gas
R: reference electrode
S: still (containing 30 ml of refluxing benzene)
W: aqueous layer

Figure 3. Apparatus for Duet electrosynthesis of benzoquinone.

with vigorous stirring (1100rpm) under the conditions of either controlled anode-potential (1.18 V vs Hg/Hg_2SO_4 electrode) or controlled current (1.3 mA cm^{-2}). The electric charge passed was 1.0 mF unless otherwise stated.

In Duet electrolysis of benzene, 3 ml of benzene added to both the anode and cathode chambers was electrolyzed under controlled cathode-potential conditions (-0.5 V vs Hg/Hg_2SO_4 electrode). The composition of the anolyte and catholyte is the same as described above. In the electrolysis with the solvent extraction, 17 and 30 ml of benzene were added to the electrolytic chamber(s) and the still(s), respectively. The still is connected to the electrolytic cell through a side-arm tube and heated so as to reflux benzene. Thus, BQ formed in the aqueous phase can be continuously extracted with benzene and transferred to the still.

Oxidation of hydroquinone with copper(II) sulfate. Into one chamber of the cell (Figure 3) was placed 100 ml of 0.2 M acetate buffer (pH 4.6) containing 0.5 mmol of HQ, 0.2 mmol of copper(II) sulfate, 5 ml of acetonitrile and 7-22 ml of benzene. After introducing O_2 gas into the solution at a rate of 10 ml min^{-1} for an hour with stirring (1100 rpm) and heating the still to reflux benzene, the reaction mixture was analyzed with HPLC.

Acknowledgment: A part of this work was supported by Grant-in-Aid for Scientific Research on Priority Area from the Ministry of Education, Science and Culture (No. 62607001).

References

1. Udupa, K. S.; Submarian, G. S.; H. V. K. Udupa Bull. Acad. Pol. Sci., **1961**, 9, 45.
2. Goodridge, F.; Umeh, E. O. Electrochim. Acta, **1975**, 20, 991.
3. Kinoshita, T.; Harada, J.; Ito, S.; Sasaki, K. Angew. Chem. Int. Ed. Engl., **1983**, 22, 502.
4. Ito, S; Okada, H.; Katayama, R.; Kunai, A.; Sasaki, K. J. Electrochem. Soc., **1988**, 135, 2996.
5. Ito, S; Yamasaki, T; Okada, H.; Okino, S.; Sasaki, K. J. Chem. Soc., Perkin Trans. 2, **1988**, 285.
6. Gorrdon, B. M.; Wahl, A. C. J. Am. Chem. Soc., **1958**, 80, 273.
7. Kirwon, J. B.; Peat, F. D.; Proll, P. J.; Sutcliffe, L. H. J. Phys. Chem., **1963**, 67, 1617.
8. Ito, S.; Kunai, A.; Okada, H.; Sasaki, K. J. Org. Chem., **1988**, 53, 296.