

# Duet electrosynthesis

## Part II: 1,4-naphthoquinone from naphthalene

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The combination of the anodic oxidation of naphthalene on a  $\text{PbO}_2$  electrode with the mediated oxidation of naphthalene in the cathode chamber using the  $\text{Cu(I)}/\text{Cu(II)}$  redox couple in a divided electrolytic cell produces 1,4-naphthoquinone with a current yield of 77%. The by-products are 1-naphthol and 2-formyl-trans-cinnamaldehyde. The pathways for the formation of these products are discussed.

### 1. Introduction

The development of an efficient electrolytic system for the oxidation of aromatic compounds to the corresponding quinone [1] has been the subject of industrial electrochemistry. Benzene is anodically oxidized to *p*-benzoquinone by use of a lead dioxide electrode with a current yield of 62% [2]. Anthracene is oxidized to anthraquinone in mediated oxidation using the  $\text{Ce(III)}/\text{Ce(IV)}$  redox couple with a current yield of 55% [3]. The current yield of 1,4-naphthoquinone (NQ) in the electrochemical oxidation on a platinum gauze anode into which was pressed a mixture of carbon and naphthalene was, however, remarkably low (30%) [4] by contrast with its analogues, although the details of the electrolytic oxidation of naphthalene have never been studied [1]. The purpose of the present work is to find a means of improving the current efficiency for NQ production. To the electrolytic oxidation of naphthalene, we have applied the paired electro-oxidation technique [5], which we term 'duet electrosynthesis' [6]. This technique allows production of the same product from a common starting material in both the anodic and cathodic chambers in a single H-shaped electrolytic cell.

### 2. Experimental details

#### 2.1. Materials and analysis

All the chemicals except for 2-formyl-trans-cinnamaldehyde (AL) were the highest grade commercial materials and were used without further purification. AL was synthesized by oxidation of naphthalene catalyzed by a  $\text{Cu-Pd/SiO}_2$  catalyst and identified by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR and MS [7]. Oxidation products were analysed with a liquid chromatogram (Hitachi 655). The separation column was a Cica-MERCK

Hibar Lichrosorb RP-18 (10  $\mu\text{m}$ ) and the eluent was a mixture of acetonitrile (50% by volume) and a 50 mM phosphate buffer of pH 3.5 (50% by volume). Using a variable wavelength u.v. monitor (Hitachi 638-41) coupled with a Shimadzu Chromatopack C-R6A integrator, 1,4-naphthoquinone (NQ), 1-naphthol (OL) and AL were determined at 320 nm.

#### 2.2. Electrolysis of naphthalene

The standard procedure was as follows. Into a conventional H-shaped glass cell (5 cm diam. and 9 cm high) divided by a cation-exchange membrane (Tokuyama Soda Neosepta CM-1) were added 100 ml of anolyte (50 ml of acetonitrile plus 50 ml of 1.0 M sulphuric acid) and 100 ml of catholyte (50 ml of acetic acid, 5 ml of acetonitrile [8, 9] and 45 ml of water) containing 20 mM of copper (II) sulphate and 100 mM of sodium acetate. The electrode materials were a commercial lead dioxide electrode deposited on titanium base (Permelec Electrode Ltd, 21  $\text{cm}^2$  geometrical surface area) as anode and a carbon rod (13 mm diam. and 16  $\text{cm}^2$  geometrical surface area) as cathode.

In the anodic oxidation, naphthalene (2.0 mmol) was electrolysed under vigorous stirring with a controlled anode potential of 1.25 V/Hg/Hg<sub>2</sub>SO<sub>4</sub> electrode [6]. The reaction on the counter electrode is the reduction of copper (II) sulphate to copper (I) species, which is reoxidized to copper (II) ions with molecular oxygen introduced at a rate of 60 ml min<sup>-1</sup>.

In the mediated oxidation of naphthalene using a  $\text{Cu(I)}/\text{Cu(II)}$  couple in the cathode chamber, 2.0 mmol of naphthalene was added to the catholyte. With a controlled cathode potential of -0.5 V/Hg/Hg<sub>2</sub>SO<sub>4</sub> electrode [8], copper (II) sulphate was electrolysed with vigorous stirring (1100 r.p.m.). During the electrolysis, oxygen gas was introduced into the catholyte at a rate

Table 1. Selectivity of 1,4-naphthoquinone in the anodic oxidation of naphthalene\*

Anode	Co-solvent	Naphthalene/mmol		Selectivity <sup>†</sup> /%			Current yield of NQ/%
		Initial	Final	NQ	AL	OL	
PbO <sub>2</sub>	Acetonitrile (50% by volume)	1.000	0.748 <sup>‡</sup>	84.4	4.2	7.7	42
PbO <sub>2</sub>	Acetic acid (50% by volume)	1.000	0.442 <sup>§</sup>	38.5	3.7	2.6	43
Pt	Acetonitrile <sup>#</sup> (50% by volume)	1.000	0.739 <sup>§</sup>	23.7	5.1	1.6	12

\* Solvent: 100 ml (50 ml of acetonitrile (or acetic acid) plus 50 ml of 1.0 M H<sub>2</sub>SO<sub>4</sub>), anode potential: 1.25 V/Hg/Hg<sub>2</sub>SO<sub>4</sub> electrode, electric charge passed: 3 mF.

<sup>†</sup> The yield of the product based on naphthalene consumed.

<sup>‡</sup> Duration of electrolysis: 1.5 h.

<sup>§</sup> Duration of electrolysis: about 6 h.

<sup>#</sup> In the presence of 50 mM Ag<sub>2</sub>SO<sub>4</sub>.

of 60 ml min<sup>-1</sup> and the current density observed was 0.7–1.3 mA cm<sup>-2</sup>. The reaction on the counter electrode is the oxidation of water to oxygen.

In the 'duet electrolysis', 20 mM naphthalene was added to both the anolyte and catholyte. With vigorous stirring, copper (II) sulphate in the cathode chamber and naphthalene in the anode chamber were electrolysed simultaneously under controlled cathode potential at -0.5 V/Hg/Hg<sub>2</sub>SO<sub>4</sub> electrode. Oxygen gas was introduced into the catholyte at 60 ml min<sup>-1</sup> during the electrolysis.

In the mediated oxidation of naphthalene under anaerobic conditions, 5.0 mM of hydrogen peroxide was added to the catholyte and copper (II) sulphate was electrolysed.

### 2.3. Gamma-ray radiolysis of naphthalene

In the gamma-ray radiolysis of aqueous naphthalene solution, 2 ml of 50% acetic acid (by volume) containing 100 mM of sodium acetate, 20 mM of naphthalene, 1 mM of EDTA, and 5% (by volume) of acetonitrile was added to a sample-tube 1.0 cm in diameter. After bubbling oxygen gas into the solution for 30 min, the solution was irradiated using a cobalt-60 gamma ray irradiator (Hiroshima University) for 2 h. The dose, measured by a Fricke dosimeter, was 5.1 kGy.

## 3. Results and discussion

### 3.1. Anodic oxidation of naphthalene

Benzene suspended in aqueous sulphuric acid was oxidized on a lead dioxide anode to give *p*-benzoquinone with 62% current yield. As demonstrated in Table 1, naphthalene, dissolved in 50% acetonitrile and in 50% acetic acid, was also anodically oxidized by use of the lead dioxide electrode, producing 1,4-naphthoquinone (NQ) with 42 and 43% current yield, respectively. Besides NQ, a small amount of 2-formyl-transcinnamaldehyde (AL) and 1-naphthol (OL) were also obtained. In the electrolysis in 50% acetonitrile, the amount of naphthalene consumed was much smaller than that in the electrolysis in 50% acetic acid, though the current yield of NQ was comparable.

Thus the selectivity (i.e. the yield of the product based on the amount of the reactant consumed) of NQ amounts to 84.4% for the anodic oxidation in 50% acetonitrile. The total selectivity of NQ plus AL plus OL was 96.3%, indicating that the oxidation of naphthalene on the PbO<sub>2</sub> anode in 50% acetonitrile is remarkably selective. The formation of acetoxyated naphthalenes [10] is probably responsible for the low selectivity of NQ in the electrolysis in 50% acetic acid.

In the indirect oxidation of naphthalene by use of a Ag<sup>+</sup>/Ag<sup>2+</sup> redox couple and a platinum electrode, both the selectivity and the current yield of NQ were low, in contrast to the case of benzene [6] and further experiment was not done.

Table 2 summarizes the effects of the electrolytic conditions, such as the anode potential, the amount of electric charge passed and the concentration of naphthalene, on the Faradaic yield of the products. In agreement with the result of the anodic oxidation of benzene on a PbO<sub>2</sub> electrode [11], the Faradaic yield of NQ increased with decreasing anode potential in the range from 1.4 to 1.0 V/Hg/Hg<sub>2</sub>SO<sub>4</sub>. The Faradaic yield of NQ was essentially constant regardless of the amount of electric charge, indicating that the consecutive oxidation of NQ was negligible.

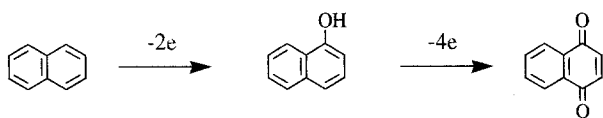
The effect of the concentration of naphthalene on

Table 2. Faradaic yield of naphthoquinone in the anodic oxidation of naphthalene\*

Anode potential /V <sup>†</sup>	Electric charge /mF	Naphthalene /mM	Faradaic yield/ mmol F <sup>-1</sup>		
			NQ	AL	OL
1.00	1.0	20	95	4	10
1.20	1.0	20	80	3	11
1.40	1.0	20	64	3	5
1.25	1.0	10	78	4	7
1.25	2.0	10	80	4	8
1.25	3.0	10	80	4	7
1.25	1.0	20	75	3	12
1.25	1.0	30	60	4	18

\* Solvent: 50 ml of acetonitrile plus 50 ml of 1.0 M H<sub>2</sub>SO<sub>4</sub>.

<sup>†</sup> Against Hg/Hg<sub>2</sub>SO<sub>4</sub> electrode.



Scheme 1. Reaction pathway for anodic oxidation of naphthalene.

the Faradaic yield of NQ is shown in Table 2. In electrolysis at constant anode potential (1.25 V) and fixed electric charge (1.0 mF), the higher the initial concentration of naphthalene, the lower the Faradaic yield of NQ. The Faradaic yield of OL, however, increased with increasing initial naphthalene concentration. These results are explained by the consecutive pathway shown in Scheme 1. The mechanism for the oxidation of aromatic compounds on  $\text{PbO}_2$  electrode has been discussed [12], but further mechanistic study was not carried out. According to Scheme 1, OL, as well as naphthalene, are oxidized on the surface of the lead dioxide electrode. With increasing initial concentration of naphthalene, the oxidation of naphthalene to OL is favoured over that of OL to NQ, changing the product distribution as shown in Table 2. Under the optimum electrolytic conditions, the Faradaic yield of NQ was  $94 \text{ mmol F}^{-1}$ , which corresponds to 57% current yield.

### 3.2. Mediated oxidation of naphthalene

In a previous paper [6], we showed that benzene suspended in aqueous acetate buffer solution is oxidized in the cathode chamber in the presence of both molecular oxygen as an oxidant and the  $\text{Cu(I)/Cu(II)}$  redox couple as mediator, giving *p*-benzoquinone and hydroquinone with Faradaic yields of 24–64 and 39–75  $\text{mmol F}^{-1}$ , respectively. Benzene is appreciably soluble ( $22 \text{ mmol dm}^{-3}$ ) in water, while naphthalene is sparingly soluble in aqueous solution (0.25 mM at  $25^\circ \text{C}$  [1]). Accordingly, the effect of co-solvent on the oxidation of naphthalene by use of a  $\text{Cu(I)/Cu(II)}$  mediator was examined initially. In contrast to the anodic oxidation of naphthalene described above, acetic acid was a better co-solvent than acetonitrile, as summarized in Table 3. In the following experiments for seeking optimum electrolytic conditions, 50% (by volume) acetic acid was used exclusively as a solvent unless otherwise stated.

Table 3. Solvent effect on oxidation of naphthalene with oxygen mediated by the  $\text{Cu}^+/\text{Cu}^{2+}$  couple\*

Solvent <sup>†</sup>	Faradaic yield/ $\text{mmol F}^{-1}$		
	NQ	AL	OL
50% Acetonitrile	trace	trace	trace
70% Acetonitrile	trace	trace	trace
50% Acetic acid	5	11	8
70% Acetic acid	6	8	7
90% Acetic acid	6	5	7

\* Naphthalene: 10 mM,  $\text{Cu}(\text{ClO}_4)_2$ : 20 mM,  $\text{LiClO}_4$ : 20 mM, electric charge: 1.0 mF.

<sup>†</sup> Expressed by volume (%) of organic solvent in aqueous solutions.

Table 4. Effect of the counter anions of copper (II) salts on the Faradaic yield of products\*

Copper (II) salt	Faradaic yield/ $\text{mmol F}^{-1}$		
	NQ	AL	OL
$\text{Cu}(\text{ClO}_4)_2$	10	10	10
$\text{CuSO}_4$	10	9	9
$\text{Cu}(\text{CH}_3\text{COO})_2$	10	9	8
$\text{Cu}(\text{OH})_2$	12	10	5

\* Naphthalene: 10 mM,  $\text{Cu(II)}$ : 20 mM,  $\text{CH}_3\text{COONa}$ : 100 mM, solvent: 50% (by volume) acetic acid, electric charge: 1.0 mF.

Four kinds of copper (II) salts are tested as a source of copper (I) species but little difference was observed among them (Table 4).

The addition of 2.5 to 7.5% (by volume) of acetonitrile to the catholyte increased the Faradaic yield of NQ up to  $25 \pm 1 \text{ mmol F}^{-1}$  in the 50% acetic acid solution, while the yield of AL increased in the 90% acetic acid solution by addition of 0.1–0.5% acetonitrile (Table 5). The primary role of acetonitrile is to stabilize copper (I) species by complexation [8, 9]. The maximum Faradaic yield of NQ ( $25 \pm 1 \text{ mmol F}^{-1}$ ) was obtained in the 50% acetic acid solution in the presence of 2.5–7.5% acetonitrile.

As shown in Table 6, the Faradaic yield of NQ increased with increasing initial concentration of naphthalene, but the highest concentration was limited to 20 mM because of its solubility. In the 90% acetic acid solution, naphthalene is soluble up to 200 mM, but the Faradaic yield of NQ was less than that obtained in the 50% acetic acid solution. The formation of AL and OL was favoured in 90% acetic acid. The effect of acetic acid on the Faradaic yield will be discussed later.

The effect of the initial concentration of copper (II) sulphate on the yield of NQ was negligible as shown in Table 7.

Table 5. Effect of acetonitrile on the Faradaic yield of naphthoquinone\*

Solvent	Acetonitrile /% by volume	Faradaic yield/ $\text{mmol F}^{-1}$		
		NQ	AL	OL
50% Acetic acid <sup>†</sup>	0	13	14	14
	1	22	37	9
	2.5	25	30	9
	5	26	23	7
	7.5	24	18	6
	10	17	11	4
	20	4	2	trace
90% Acetic acid <sup>‡</sup>	0	16	23	30
	0.05	14	41	19
	0.1	15	50	18
	0.5	22	48	16
	5	trace	1	trace

\* Electric charge passed: 1.0 mF.

<sup>†</sup> Naphthalene: 20 mM,  $\text{CuSO}_4$ : 20 mM,  $\text{CH}_3\text{COONa}$ : 100 mM.

<sup>‡</sup> Naphthalene: 100 mM,  $\text{Cu}(\text{ClO}_4)_2$ : 20 mM,  $\text{LiClO}_4$ : 100 mM.

Table 6. Effect of concentration of naphthalene on the Faradaic yield of naphthoquinone\*

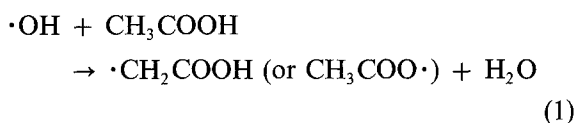
Solvent	Naphthalene /mM	Faradaic yield/mmol F <sup>-1</sup>		
		NQ	AL	OL
50% Acetic acid <sup>†</sup>	5	10	8	3
	10	18	15	5
	20	26	23	7
90% Acetic acid <sup>‡</sup>	10	6	5	7
	50	14	18	21
	100	16	23	30
	200	16	24	33

\* Electric charge passed: 1.0 mF.

<sup>†</sup> CuSO<sub>4</sub>: 20 mM, CH<sub>3</sub>COONa: 100 mM, acetonitrile: 5% by volume.<sup>‡</sup> Cu(ClO<sub>4</sub>)<sub>2</sub>: 20 mM, LiClO<sub>4</sub>: 100 mM, acetonitrile: 5% by volume.

In Table 8 the effect of the pH and the concentration of the supporting electrolyte (sodium acetate) on the Faradaic yield of NQ are summarized. At the fixed concentration of sodium acetate (100 mM), the optimum pH for the formation of NQ ranged from 1.5 to 2.5.

In summary, the maximum Faradaic yield of NQ was as low as  $27 \pm 1$  mmol F<sup>-1</sup>, even under the optimum electrolytic conditions. The total Faradaic yield of NQ plus AL plus OL was 56–71 mmol F<sup>-1</sup>, which is about half that (112–118 mmol F<sup>-1</sup>) in the mediated oxidation of benzene suspended in 0.2 mmol dm<sup>-3</sup> acetate buffer of pH 4.6 [6]. It is plausible that the large amount of acetic acid, which was added as a co-solvent in the mediated oxidation of naphthalene, deactivates hydroxyl radicals according to the following:



Provided that naphthalene and acetic acid competitively react with hydroxyl radical, the yield of NQ, AL and OL increase with increasing initial concentration of naphthalene. The result in Table 6 suggests that the low Faradaic yield observed in the mediated oxidation of naphthalene is, at least partly, due to the deactivation Reaction 1.

The reaction of benzene with hydroxyl radical is

Table 7. Effect of copper (II) sulphate on the Faradaic yield of naphthoquinone\*

CuSO <sub>4</sub> /mM	Faradaic yield/mmol F <sup>-1</sup>		
	NQ	AL	OL
5	26	31	11
10	28	28	9
15	27	26	8
20	26	23	7
25	26	23	8

\* Solvent: 50% (by volume) acetic acid, naphthalene: 20 mM, CH<sub>3</sub>COONa: 100 mM, acetonitrile: 5% by volume, electric charge: 1.0 mF.

Table 8. Effect of concentrations of sodium acetate and hydrogen ions on the Faradaic yield of naphthoquinone\*

CH <sub>3</sub> COONa/mM	pH	Faradaic yield/mmol F <sup>-1</sup>		
		NQ	AL	OL
50	2.2	25	26	9
75	2.3	25	20	7
100	1.5 <sup>†</sup>	28	33	10
100	2.0 <sup>†</sup>	27	29	10
100	2.5	26	23	7
100	3.0 <sup>‡</sup>	24	22	6
100	3.5 <sup>‡</sup>	17	19	5
100	4.0 <sup>‡</sup>	12	16	6
150	2.6	21	17	5
200	2.7	19	16	4

\* Solvent: 50% (by volume) acetic acid, naphthalene: 20 mM, CuSO<sub>4</sub>: 20 mM, acetonitrile: 5% by volume, electric charge: 1.0 mF.<sup>†</sup> pH was adjusted by addition of aq. H<sub>2</sub>SO<sub>4</sub>.<sup>‡</sup> pH was adjusted by addition of aq. NaOH.

generally accepted to be diffusion-controlled [13] with a large rate constant of  $(4-8) \times 10^9$  mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup>. In a diffusion-controlled reaction, the magnitude of the rate constant is mainly determined by the probability of the encounter between the two reactants. For example, the rate constant for the reaction of hydroxyl radical with ethylalcohol and isopropylalcohol is almost equal ( $2.1 \times 10^9$  and  $2.0 \times 10^9$  mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup>, respectively) [14], though the latter has a hydrogen atom on the secondary carbon atom. On a benzene ring there are six equivalent positions to be attacked by a hydroxyl radical, while there are only four  $\alpha$ -positions in a naphthalene molecule. Since the molecular size of naphthalene is approximately twice that of benzene, the probability of the encounter between the  $\alpha$ -positions of the naphthalene molecule and a hydroxyl radical is estimated to be about one-third that between the six equivalent positions of benzene and hydroxyl radical. The rough estimation of the difference in the reactivity of benzene and naphthalene toward hydroxyl radicals can reasonably explain the low Faradaic yields of NQ, AL and OL observed in the mediated oxidation of naphthalene.

### 3.3. Duet electrosynthesis of naphthoquinone

The combination of these anodic and cathodic reactions in a divided electrolytic cell constitutes an efficient electrolytic system, which we named 'duet electrosynthesis'. As demonstrated in Table 9, NQ was formed from naphthalene in both the anodic and cathodic chambers simultaneously with a total Faradaic yield of 124–129 mmol F<sup>-1</sup>, which corresponds to 74–77% of the current yield. In contrast to the duet electrolysis of benzene [6], 1,4-naphthohydroquinone is readily oxidized to NQ under the present electrolytic conditions and continuous solvent extraction was unnecessary. The duet electrolysis in Table 9 was done under controlled cathode potential at  $-0.5$  V/Hg/Hg<sub>2</sub>SO<sub>4</sub> [8]. The observed anode potential during the

Table 9. Duet electroynthesis of 1,4-naphthoquinone from naphthalene

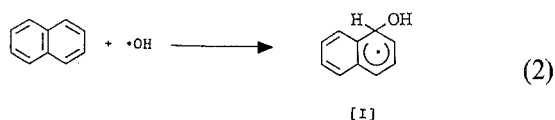
Electric charge /mF	Products/ $\mu\text{mol}$						Faradaic yield of NQ /mmol F <sup>-1</sup>		
	Anode			Cathode			Anode	Cathode	Total
	NQ	AL	OL	NQ	AL	OL			
1.0	101	3	7	28	25	8	101	28	129
3.0	299	9	15	80	80	21	100	26	126
5.0	491	17	19	128	126	29	98	26	124

duet electrolysis was in the range 0.95 to 1.0 V/Hg/Hg<sub>2</sub>SO<sub>4</sub>, which lies in the optimum anode potential range shown in Table 2.

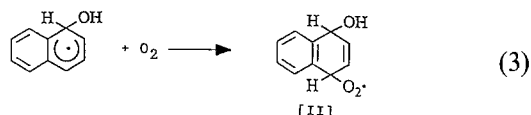
### 3.4. Reaction pathway in the mediated oxidation of naphthalene

The electrolytic oxidation of benzene mediated by the Cu(I)/Cu(II) redox couple proceeds through a hydroxycyclohexadienyl radical [13], which is formed by an addition reaction of hydroxyl radical to the benzene nucleus [15]. The radical formed is then oxidized with molecular oxygen or copper (II) ion to give phenol, hydroquinone, and *p*-benzoquinone. The reaction scheme for the formation of these products has been published [9, 13, 16]. In the mediated oxidation of naphthalene, the reaction scheme (Scheme 2) is essentially the same as that in the oxidation of benzene.

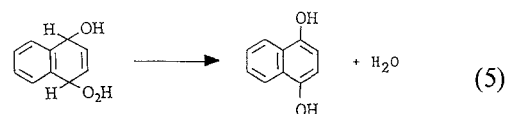
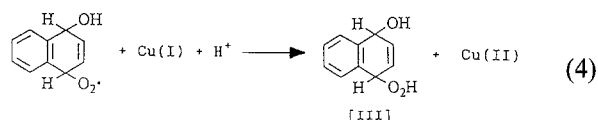
The first step of the oxidation of naphthalene is the addition reaction of the hydroxyl radical to the 1-position of naphthalene to give a radical [I].



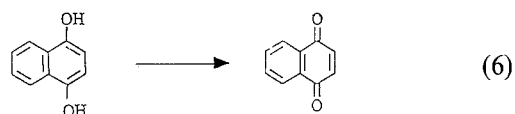
NQ is mainly produced via a 4-peroxy radical [II], which is formed by addition of dioxygen to the radical [I].



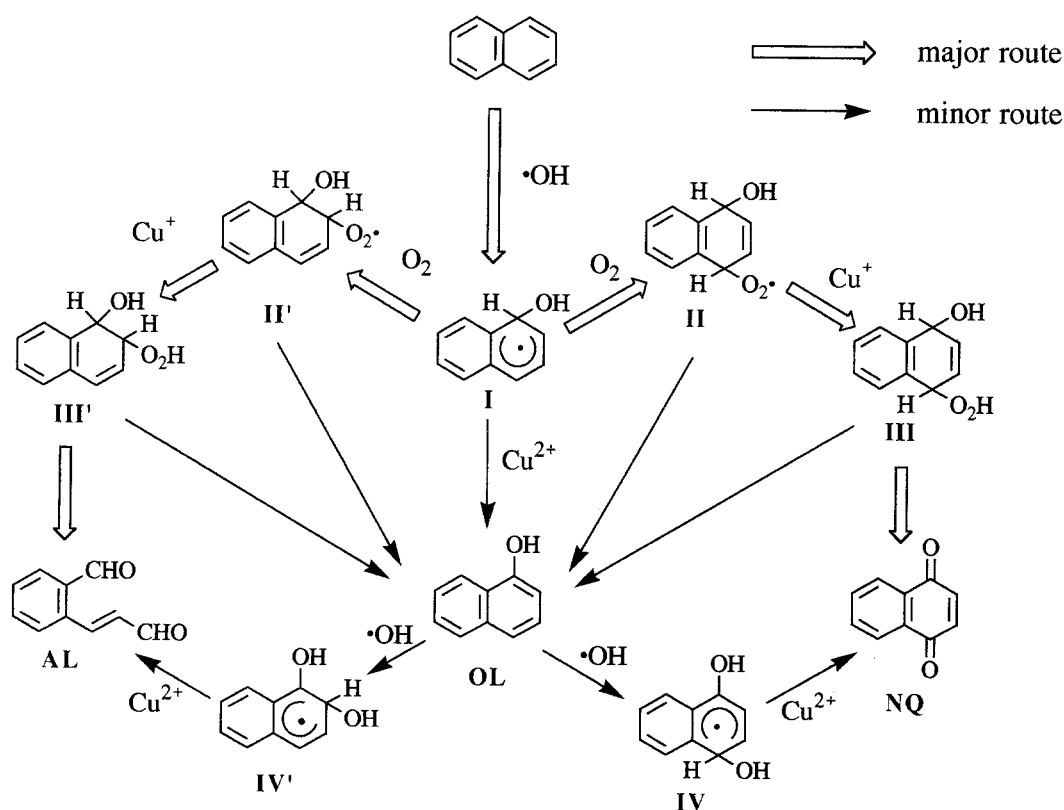
The reduction of the peroxy radical [II] to the corresponding hydroperoxide [III] with copper (I) species followed by dehydration gives 1,4-naphthohydroquinone,



which is, in turn, readily oxidized to NQ with copper (II) ions and/or O<sub>2</sub>.



An alternative route to NQ is a consecutive oxidation of OL with the hydroxyl radical. The latter pathway is not plausible, however, since the Faradaic yield of NQ



Scheme 2. Reaction pathway for mediated oxidation of naphthalene.

Table 10. Oxidation of naphthalene and related compounds with oxygen or H<sub>2</sub>O<sub>2</sub> mediated by the Cu(I)/Cu(II) couple\*

Oxidant	Reactant	Concentration /mM	Faradaic yield/mmol F <sup>-1</sup>			
			NQ	AL	OL	2-Me-NQ
O <sub>2</sub>	Naphthalene	20	26	23	7	—
H <sub>2</sub> O <sub>2</sub> <sup>†</sup>	Naphthalene	20	32	9	107	—
O <sub>2</sub>	1-Naphthol	10	34	3	—	—
H <sub>2</sub> O <sub>2</sub> <sup>†</sup>	1-Naphthol	20	25	1	—	—
O <sub>2</sub>	2-Naphthol	10	trace	trace	—	—
O <sub>2</sub>	2-Methyl-naphthalene	20	—	—	—	8
O <sub>2</sub> <sup>‡</sup>	Naphthalene	20	3.7 <sup>§</sup>	5.4 <sup>§</sup>	5.0 <sup>§</sup>	—

\* Solvent: 50% (by volume) acetic acid, CuSO<sub>4</sub>: 20 mM, acetonitrile: 5% by volume, electric charge: 1.0 mF.

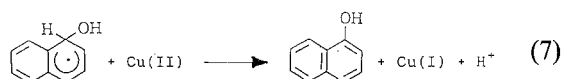
<sup>†</sup> H<sub>2</sub>O<sub>2</sub>: 5.0 mM, atmosphere: N<sub>2</sub>.

<sup>‡</sup> Irradiated with gamma-ray with dose of 5.1 kGy in the absence of CuSO<sub>4</sub>.

<sup>§</sup> Yield of products (μmol) per dose of 5.1 kGy.

is almost constant, regardless of the electric charge passed, as shown in Table 9. If the consecutive route is dominant, the Faradaic yield of NQ should increase with increasing duration of electrolysis.

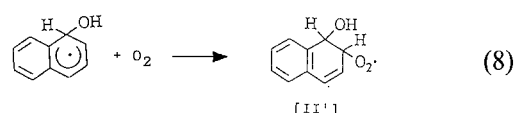
Three pathways for the formation of OL are possible. One is the direct oxidation of the radical [I] with the copper (II) ion.



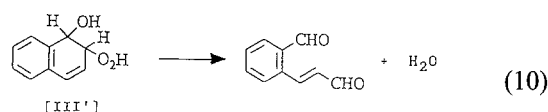
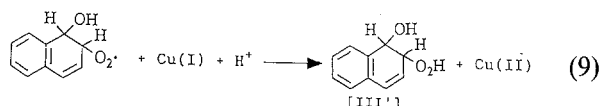
Alternatively, OL can be formed by elimination of hydroperoxy radical ( $\cdot\text{OOH}$ ) or hydrogen peroxide from the 4-peroxy radical [II] or from the 4-hydroperoxide [III], respectively. Reaction 7 can be ruled out, since the relative yield of OL to NQ was almost constant when the initial concentration of copper (II) sulphate was increased from 5 to 25 mM, as shown in Table 7. If Reaction 7 is solely responsible for the formation of OL, the relative yield of OL to NQ should increase with increasing concentration of copper (II) ions. The main pathway(s) for OL formation is, therefore, II  $\rightarrow$  OL and/or III  $\rightarrow$  OL.

Some experiments were done to elucidate the pathway to AL from naphthalene, since mucondialdehyde(s), the benzene analogue of AL, was not appreciably formed in the mediated oxidation of benzene [13, 17]. One might consider that AL was produced by a consecutive oxidation of 2-naphthol, which was produced from naphthalene. The mediated oxidation of 2-naphthol instead of naphthalene in similar electrolytic conditions, however, gave only a trace amount of AL, as shown in Table 10.

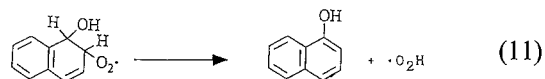
Likewise, a small amount of AL was obtained by the mediated oxidation of 1-naphthol, indicating that AL is formed via neither 1- nor 2-naphthol. As clearly demonstrated in Table 10, anaerobic oxidation of naphthalene with hydrogen peroxide and electro-generated copper (I) species gave a trace amount of AL, and an appreciable amount of AL can be obtained only when naphthalene is oxidized with oxygen. These results can be explained by the formation of the 2-peroxy radical [II'] according to Reaction 8.



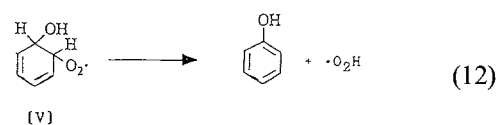
The reduction of the 2-peroxy radical [II'] to 2-hydroperoxide [III'] with copper (I) species followed by dehydration gives AL.



One may ask why AL is formed in the mediated oxidation naphthalene, while mucondialdehyde is not appreciably formed in the oxidation of benzene [13, 17]. In the oxidation of benzene with hydroxyl radicals, hydroquinone is produced only when both oxygen and copper (I) ions are present in the reaction system [16]. In the gamma-ray radiolysis of aqueous benzene solution saturated with oxygen gas, the main product was phenol with a small amount of hydroquinone (about 5% of phenol) [16]. As shown in Table 10, gamma-ray radiolysis of naphthalene in the 50% acetic acid gave comparable amounts of NQ, AL and OL. A possible explanation of these results is as follows. The elimination reaction of O<sub>2</sub>H from the peroxy radical [II'] to give OL



is much slower than that from a 2-peroxy radical [V] derived from benzene.



which was originally proposed by Dorfman and coworkers [14]. The long life-time of the peroxy radical [II'] enables the occurrence of Reaction 9 to give AL.

According to the pathways described above, NQ

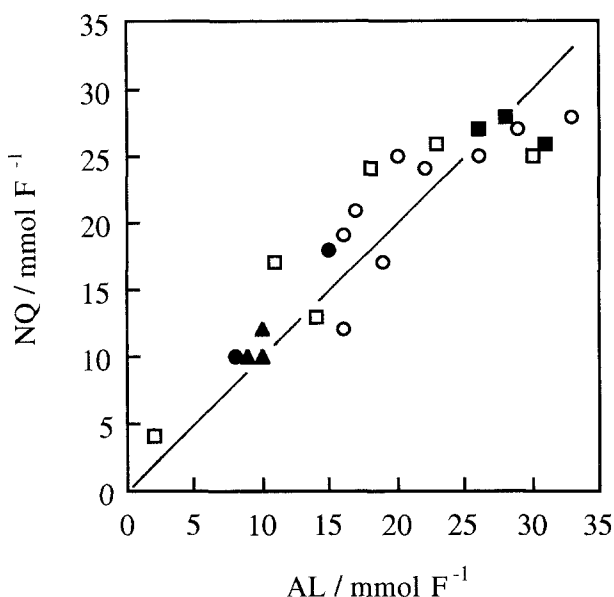


Fig. 1. Plot of yield of NQ against yield of AL. (▲) From Table 4, (□) from Table 5, (●) from Table 6, (■) from Table 7, (○) from Table 8.

and AL were competitively formed via a common intermediate [I]. Since the molar ratios of NQ to AL obtained should be determined by the relative rates of Reactions 3 to 8, the relative yield of NQ to AL shown in Tables 3–8 was examined further.

The plot of the yield of NQ against that of AL in Fig. 1 shows that the yield of NQ is proportional to that of AL, independent of the reaction conditions, provided that the solvent was fixed at 50% acetic acid. Likewise the yield of OL is proportional to that of AL as shown in Fig. 2, indicating that OL and NQ (and AL) are formed through a common intermediate. The

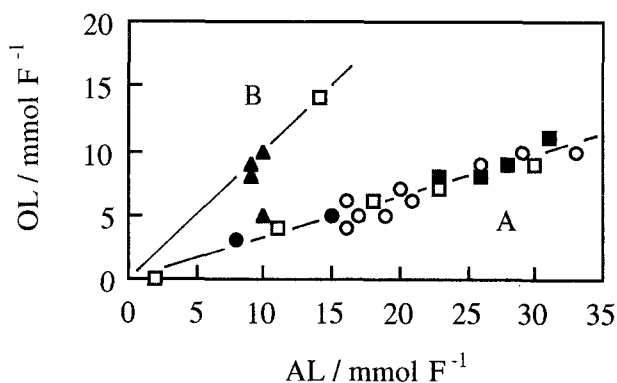


Fig. 2. Plot of yield of OL against yield of AL in the presence (A) and absence (B) of acetonitrile. Symbols are the same as in Fig. 1.

possible common intermediate for the formation of OL and NQ (and AL) should be either [II]/[II'] or [III]/[III']. At the present stage of the investigation, one cannot discriminate the pathway [I] → [II] → OL from the pathway [I] → [II] → [III] → OL.

#### 4. Conclusion

The maximum Faradaic yield of NQ obtained in the 'duet electroynthesis' of naphthalene was 124–129 mmol F<sup>-1</sup> (current yield of 74–77%), which corresponds to the sum of those (95 and 26–28 mmol F<sup>-1</sup>) in the anodic (Table 2) and the mediated oxidations (Table 7) performed separately. The result suggests the Duet electroynthesis is a promising method for the production of NQ from naphthalene.

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