Electrolytic Reduction of Sulfochlorides under Controlled Potential (Rep. II)*

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In a previous report, studies on the electrolytic reduction of sulfochlorides having a different substituent, and in this paper, studies on the electrolysis of other sulfochlorides having another reducible radical i.e. NO_2 or SO_2Cl , besides a SO_2Cl , which shows respectively a different irreversibility polarographically were made. For the preparation of some intermediate products such as sulfinic acid, disulfoxide, disulfide and thiophenol in pure state and good yield, suitable conditions of electrolytic solution and cathode potential were researched. Especially there were no polarographic data³⁾ for the second and third wave of *m*-nitrobenzene-sulfochloride, and therefore electrolytic conditions of this compound were decided by referring to other sulfochlorides.

The apparatus and electrolytic method were the same as that in the previous paper.¹⁾ The amounts of electricity, which were measured by a large gas coulometer, show a good agreement with the result of graphical integration of current and time in Fig. 1 and 2.

The separation of products were operated as a principle by the method which was shown in Table 1 in the previous paper¹⁾, but in each experiment a suitable method were employed according to the property of respective products.

Fig. 1 Current and time in electrolysis of *m*-benzene-disulfochloride.

Fig. 2 Current and time in electrolysis of *m*-nitrobenzene-sulfochloride.

The confirmation of products⁶⁾ were made as follows; *m*- $\text{C}_6\text{H}_4-(\text{SO}_2\text{H})_2$ was reacted with dilute H_2SO_4 and NaNO_2 to produce *m*-phenylene-disulfo-hydroxylamin $\text{C}_6\text{H}_4: (\text{SO}_2-\text{N}(\text{OH})-\text{SO}_2)_2: \text{C}_6\text{H}_4^{(2), (4)}$, which decomposed at 212°C instead of melting; $\text{C}_6\text{H}_4: (\text{SO}_2-\text{S})_2: \text{C}_6\text{H}_4^{(5)}$ was reacted with conc. HNO_3 to analyse S content, which was 37.11% while theoreticall value is 37.21%; similarly, for $\text{C}_6\text{H}_4: (\text{S}-\text{S})_2: \text{C}_6\text{H}_4^{(2), (7)}$, S content was 45.17% while theoreticall value is 45.75%; for *m*- $\text{C}_6\text{H}_4: (\text{SH})_2$, it was reacted with acetic acid and lead acetate solution to produce Pb-salt, which was coloured light orange;

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Table 1 Reduction of *m*-benzene-disulfochloride, *m*-C₆H₄(SO₂Cl)₂ (0.01 mol/l, 2.75 g/l)

Exp. No.	14	15	16	17	18	19	20
Support. elect. medium	Brit. buff. pH 5.72	2 <i>n</i> -H ₂ SO ₄	Brit. buff. pH 5.72	"	"	2 <i>n</i> -H ₂ SO ₄	"
Added org. Solvent	20% isopropyl-alcohol	"	"	"	"	"	"
Added inorg. Solvent	—	—	0.1 mol NaCl	—	0.1 mol NaCl	"	—
Cathode potential	1.00	1.20	1.40	"	1.68 (H ₂)	1.47(")	" (")
Initial current (mA)	330	760	640	590	820	1180	1100
Final current (mA)	110	340	210	180	390	410	390
Time (hr. min.)	5 hr.-10 m.	2-50	3-50	3-20	4-40	2-45	2-05
mA × h	1120	1170	1640	1370	2010	2070	1480
Products (g)							
R-(SO ₃ H) ₂	—	—	—	—	—	—	—
R-(SO ₂ H) ₂	1.8	1.8	0.1	1.2	0.1	0.1	1.2
R: (SO ₃ -S) ₂ : R	—	—	1.4	1.4 ₅	1.1	1.0	0.4
R: (S-S) ₂ : R	—	—	—	—	0.3	0.4	0.1
R: (SH) ₂	—	—	—	—	—	—	—
Electron ratio							
4 <i>m</i> ₁	3.49	3.49	0.19	2.33	0.19	0.19	2.33
6 <i>m</i> ₂	—	—	4.86	1.56	3.81	3.47	1.38
10 <i>m</i> ₃	—	—	—	—	2.13	2.84	0.7
<i>f m</i> _{<i>f</i>}	0.51	0.51	0.57	0.63	0.41	0.36	0.46
<i>n'</i> (sum)	4.00	4.00	5.62	4.52	6.54	6.86	4.87
<i>n</i> (calculated from <i>m A</i> × <i>h</i>)	4.18	4.35	6.12	5.09	7.49	7.74	5.52
<i>I A</i>	0.18	0.35	0.50	0.57	0.95	0.88	0.65

m-NO₂-C₆H₄-SO₂H^(8),9) was of needle-like crystal and m.p. 98°C; *m*-NH₂-C₆H₄•SO₂-S•C₆H₄-NH₂⁽¹¹⁾ was of needle-like crystal and decomposed to carbon at 200°C without melting, and changed to needle containing 2HCl for the purpose of analysis, which gave the result of S content 17.76% (to theoretical value 18.13%) and Cl content 19.57% (to theoretical one 20.01%) *m*-NH₂-C₆H₄•S-S•C₆H₄-NH₂^(2),12) was needle and m.p. 59~60°C; *m*-NH₂-C₆H₄-SH⁽¹³⁾ was reacted with acetic acid and lead acetate solution to produce Pb-salt, which was coloured yellow; *m*-NH₂•C₆H₄•SO₂H⁽¹⁰⁾ decomposed at 210°C.

Thus, the following points have been made clear;

(1) Three reduction stages, shown by the polarogram of *m*-benzene-disulfochloride and not detected by that of *m*-nitrobenzene-sulfochloride in the previous paper³⁾, are due to the reduction to sulfinic acid, disulfoxide and disulfide. (Table 1 and 2)

(2) For the preparation of *m*-benzene-disulfinic acid, the use of 2 *N*-H₂SO₄ and alcoholic electrolyte and the cathode potential at -1.20 V are suitable the use of neutral solution was unsuitable, because the electrolysis some of sulfonic acid was produced and -1.00 V of the cathode potential -1.00 V must be held. And the time of electrolysis in acidic solution is shorter than that in neutral one. (Exp. 14 and 15, Fig. 2)

(3) The action of repressing the first step reduction, increases with addition of 0.1 mol NaCl and seems to influence to the second stage reduction, and therefore the product of the third stage reduction increases. (Exp. 16, 18, 19, 23, 24, 25, 26)

(4) *m*-Benzene-resorcin begins to form after formation of 0.02~0.03 mol/l C₆H₄: (S-S)₂: C₆H₄• (Exp. 18, 19, 20). And it seems that the formation velocity of *m*-amino-thiophenol from disulfide was very slowly. (Exp. 24, 25, 26)

(5) It seems that the formation of disulfoxide from sulfinic acid was difficult, while the formation of disulfide from disulfoxide was easy. (Exp. 17, 20)

(6) Only in neutral solution and -0.6 V of cathode potential, *m*-nitro-benzene-sulfinic acid is able to be produced. (Fig. 1 and Exp. 21)

Table 2 Reduction of *m*-nitrobenzene-sulfochloride, *m*-NO₂-C₆H₄-SO₂Cl
(0.01 mol/l, 2.22 g/l)

Exp. No.	21	22	23	24	25	26
Support. elect. medium	Brit. buff. pH 5.72	2 <i>n</i> -H ₂ SO ₄	Brit. buff. pH 5.72	0.1 <i>n</i> -HCl	2 <i>n</i> -H ₂ SO ₄	Brit. buff. pH 5.72
Added org. solvent	20% ethyl alcohol	"	"	"	"	"
Added inorg. substance	—	—	0.1 mol NaCl	—	0.1 mol NaCl	"
Cathode potential	0.60	1.00	1.40	1.50 (H ₂)	1.47(*)	1.68(*)
Initial current (mA)	300	790	700	1020	1220	1060
Final current (mA)	160	310	220	340	580	540
Time (hr. min.)	3-50	5-00	5-35	6-20	6-30	6-40
mA × h	570	2370	2660	3340	3440	3370
Products (g)						
NO ₂ -, NH ₂ -R-SO ₃ H	—	—	—	—	—	—
NO ₂ -R-SO ₂ H	1.5	—	—	—	—	—
NH ₂ -R-SO ₂ H	—	1.4	—	—	—	—
NH ₂ -R-SO ₂ -S-R-NH ₂	—	—	1.20	—	—	—
NH ₂ -R-S-S-R-NH ₂	—	—	—	1.0	1.0	1.0
NH ₂ -R-SH	—	—	—	—	—	—
Electron ratio						
2 <i>m</i> ₁	1.60	—	—	—	—	—
8 <i>m</i> ₂	—	7.21	—	—	—	—
9 <i>m</i> ₃	—	—	7.71	—	—	—
11 <i>m</i> ₄	—	—	—	8.87	8.87	8.87
<i>f m</i> _f	0.40	0.71	1.29	2.13	2.13	2.13
<i>n'</i> (sum)	2.00	8.00	9.00	11.00	11.00	11.00
<i>n</i> (calculated from mA × h)	2.12	8.83	9.91	12.46	12.83	12.58
<i>Δ A</i>	0.12	0.83	0.91	1.46	1.83	1.58

(7) Sulfonic acid is not occurred only for *m*-nitrobenzene-sulfochloride, while all other sulfochlorides produce a small amount of sulfonic acid. (Exp. 21~26)

(8) For *m*-benzene-disulfochloride, the electron ratio of the 1st, 2nd and 3rd step reduction, calculated from the amount of products, is 3:2:1 in the absence of Cl⁻ (Exp. 20). When a combination wave of 2nd and 3rd steps reduction with H₂ wave appeared in polarogram of acidic solution, the ratio of 2nd and 3rd steps changes with the concentration of Cl⁻ as follows; 2:0.953 in absence of Cl⁻ and 2 *n*-H₂SO₄ (Exp. 2), 2:1.03 in 0.05 mol Cl⁻ and pH 2 (Exp. 5), and 5:4 in 0.1 mol Cl⁻ and 2 *n*-H₂SO₄, while for *p*-Cl-benzene-sulfochloride (Exp. 13) the ratio was 3:2.20 in 0.1 mol Cl⁻ and 2-H₂SO₄. When the separating wave of 2nd and 3rd steps appeared in the neutral solution, the ratio is 5:4 even in the condition of 0.1 mol. (Exp. 18, 19). The results as to the value of *Δ A*, is same as that of previous paper⁽¹⁾, (Table 1 and 2)

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Literature :

- (1) N.Urabe, K.Yasukochi, *This Journal* **25**, 17 (1957).
- (2) Tamm, Fichter, *Berichte* **43**, 3032 (1910).
- (3) N. Urabe, K.Yasukochi, *This Journal* **24**, 360 (1956).

Fig. 3 Half wave potential of 1st. step of SO₂Cl and NO₂ v.s. pH of electrolytic solution.

- (4) T. Suzuki, *J. Chem. Soc. Abst.* **94**, 871 (1908).
 - (5) Troeger u. Meine, *J. Pr. Chem.* **68**, 318 (1903).
 - (6) Atsushi Fujita, "Systematic Qualitative Analysis of Organic Comp."
 - (7) Zincke u. Krüger, *Berichte* **45**, 3468 (1912).
 - (8) Flürscheim, *J. Pr. Chem.*, **71**, 527 (1906).
 - (9) Limpricht, *Annalen*, **278**, 243 (1893), *Berichte* **25**, 3477 (1892).
 - (10) Limpricht, *Annalen* **278**, 252 (1893).
 - (11) Limpricht, *ibid.* **278**, 255~256 (1893).
 - (12) Zincke u. Miller, *Berichte* **46**, 784 (1913).
 - (13) Leuckart u. Holtzapfel, *J. Pr. Chem.*, **41**, 199 (1890).
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