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80. **Takao Iwaguchi** : Nonaqueous Polarography of Quinones. VI.[*1]. Polarography of Linear Aromatic *p*-Quinones.

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Linear aromatic *p*-quinones, especially 1,4-anthraquinone, 5,12-naphthacenequinone, and 6,13-pentacenequinone, have not been studied polarographically until recently, since the first one is more easily reduced at dropping mercury electrode and others are very sparingly soluble in usual polarographic media. Fortunately, Tada, *et al.*1) reported studies on the nonaqueous polarography of several quinones in glacial acetic acid containing 0.25*N* ammonium acetate because glacial acetic acid was found to be a favorable solvent for polarography of quinones in a previous work. As one of a series of studies on the nonaqueous polarography of quinones in relation to researches for carcinogens, the present experiment was carried out under identical conditions described in previous papers, and the half-wave potential and diffusion current were satisfactorily measured.

Comparison of measured half-wave potentials of *p*-quinones with those already reported for *p*-quinones showed that 1,4-anthraquinone was more easily reduced than 9,10-anthraquinone, and linear aromatic *p*-quinones (5,12-naphthacenequinone, 6,13-pentacenequinone) were less easily reduced than the corresponding angular *p*-quinones (benz[*a*]anthracene-7,12-quinone, dibenz[*a,h*]anthracene-7,14-quinone). For linear aromatic *p*-quinones, it was found that the relationship between their structure and half-wave potential agreed with the resonance theory.

Experimental

Apparatus——Instrument : Polarograph used was Yanagimoto PB-4 type (1956).
Capillary : $m^{2/3}t^{1/6}=2.195$.
Reference electrode : SME for 1,4-anthraquinone, SCE for 5,12-naphthacenequinone and 6,13-pentacenequinone, and a mercury electrode for the measurement of all diffusion current.
Electrolysis cell : $E_{1/2}$ was measured by the use of H-type cell reported in previous papers1) and i_d was measured by the use of usual polarographic cell with a mercury pool.

Reagents——1) 1,4-Anthraquinone2) : Yellow crystals, m.p. 190°(decomp.). Prepared from 1-aminoanthracene (from 1-amino-9,10-anthraquinone) by diazo coupling, reduction with $SnCl_2$, oxidation with $FeCl_3$ in AcOH, 1,4- and 1,2-anthraquinones were separated by passing their benzene solution through $CaHPO_4$ column, and recrystallized from the mixed solvent of EtOH and H_2O.
2) 5,12-Naphthacenequinone3) : Yellow-brown crystals, m.p. 271~272°(decomp.). Prepared from naphthalene and *o*-phthalic anhydride by the Friedel-Crafts reaction and recrystallized from glacial AcOH.

[*1] Part V : This Bulletin, **6**, 425 (1958).
[*2] Kita-4-bancho, Sendai (岩口孝雄).
1) M. Ishidate, K. Tada, *et al.* : This Bulletin, **2**, 266, 270, 272 (1954); **3**, 310 (1955); **6**, 425 (1958).
2) I. J. Pisovschi : Ber., **41**, 1434 (1908); K. Lagodzunski : *Ibid.*, **39**, 1717 (1906).
3) T. Tsunoda : Yûki Gôsei Kagaku Kyôkaishi, **9**, 127 (1951).

3) 6,13-Pentacenequinone[4]: Yellow-brown crystals, m.p. 370~371°(decomp.). Prepared by condensation of cyclohexane-1,4-dione and *o*-phthalaldehyde, and recrystallized from nitrobenzene.
4) Glacial AcOH : Purified by repeated fractional distillation and freezing after standing with CrO_3 for 3 days.
5) $(NH_4)_2SO_4$: Special grade supplied by the Kanto Reagent Co. was used without any purification after drying over conc. H_2SO_4 in a desiccator, m.p. 112~112.5°.

Procedure——Preparation of cell solution, correction for potential drop, removal of O_2, and others were carried out under identical conditions as described in previous papers.[1] Half-wave potential ($E_{1/2}$) and diffusion current (i_d) were measured at 25°±0.2°.

Results

1,4-Anthraquinone (I)

The maximum wave of (I) appeared in glacial acetic acid medium. The maximum wave was suppressed by addition of 0.01% cellulose acetate or 0.5% of water in a final concentration into each cell solution. It is very interesting that water can be used as one of the maximum suppressor, but the reason for it is still unknown. The polarogram of (I) in acetic acid medium containing approximately 0.5% of water is shown in Fig. 1 and by addition of water into the acetic acid medium, diffusion current constant (I_D) decreased as shown in Table I. The half-wave potential ($E_{1/2}$) was satisfactorily measured by using saturated mercurous sulfate electrode (SME) as reference electrode instead of saturated calomel electrode (SCE), and the half-wave potential ($E_{1/2}$) corrected for potential drop,[1] which was caused by the inner resistance through the circuit, was calculated as +0.027 v. vs. SCE. There was no apparent effect upon the half-wave potential by the presence of water to the extent of 1% in final concentration in each cell solution. The log i/i_d-i was then plotted against various potential vs. SME over corrected wave, giving the diagram shown in Fig. 2, whose slope is 1.66, showing that the polarographic reduction in this medium was a typical reversible one involving two-electron exchange per molecule.

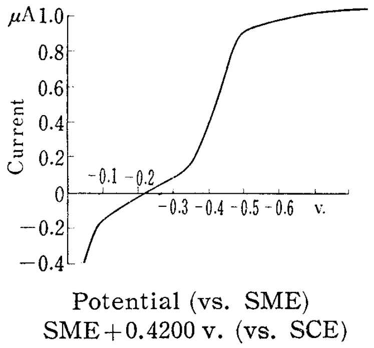

Fig. 1. Current Potential Curves (25°±0.2°)
Recorded wave

cell resistance : $6.02 \times 10^4\,\Omega$
concentration : $3.305 \times 10^{-4}\,M/L$

Table I. Effect of Addition of Water upon Diffusion Current Constant of (I)

concn. $\times 10^{-4}M$	i_d (μA)	$\frac{i_d}{cm^{2/3}t^{1/6}}$	Max. suppressor
3.447	2.461	3.194	0.01% Cellulose-acetate
3.675	2.454	3.169	0.5% H_2O
3.750	2.361	2.983	0.5% H_2O 0.01% Gelatine
3.639	2.212	2.893	1.5% H_2O
3.192	1.372	1.963	3.5% H_2O

i_d : diffusion current
$\frac{i_d}{cm^{2/3}t^{1/6}}$: diffusion current constant
% : final concentration %

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[4] W. Ried : Angew. Chem., **65**, 601 (1953).

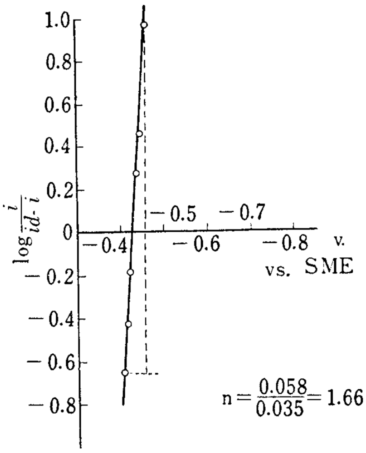

Fig. 2. Log i/i_d-i—Voltage

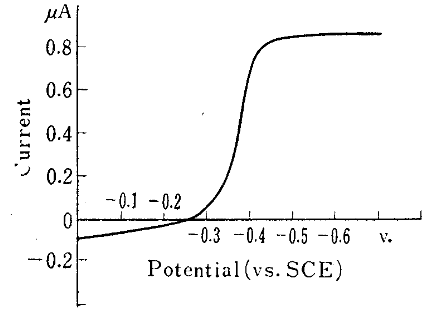

Fig. 3. Current-Potential Curves (25°±0.2°)
Recorded wave

cell resistance : $2.68\times10^4\,\Omega$
concentration : $3.323\times10^{-4}\,M/L$

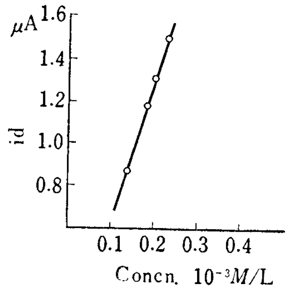

Fig. 4. Calibration Curve (25°±0.2°)

TABLE II.

concn. $10^{-4}\,M$	i_d (μA)	$\frac{i_d}{cm^{2/3}t^{1/6}}$
2.175	1.488	2.985
1.322	0.879	2.898
1.861	1.198	2.805
1.983	1.289	2.836

5,12-Naphthacenequinone (II)

The polarogram of (II) taken against SCE is shown in Fig. 3, where a well-defined, one-step reduction wave appears with $E_{1/2}$ corrected for potential drop at −0.345 v. vs. SCE. The linear relationship between concentration and diffusion current (i_d) is shown in Fig. 4, and I_D of 2.881 was obtained as the mean value of those given in Table II. The log i/i_d-i is plotted in Fig. 5 as in the case of (I), giving a slope of 1.87, indicating that the reduction was reversible, involving two-electron exchange per molecule.

6,13-Pentacenequinone (III)

(III) is sparingly soluble even in glacial acetic acid medium. The polarogram of (III) taken against SCE is shown in Fig. 6. In concentration of $10^{-5}M$, $E_{1/2}$ and I_D, as in the

TABLE III.

concn. $10^{-5}\,M$	i_d 10^{-7} A	$\frac{i_d}{cm^{2/3}t^{1/6}}$
6.453	3.946	2.856
4.302	2.590	2.803
7.763	4.724	2.831

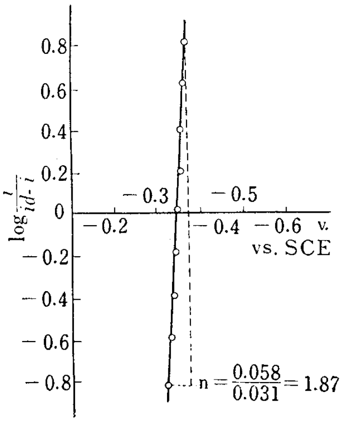

Fig. 5. Log i/i_d-i—voltage

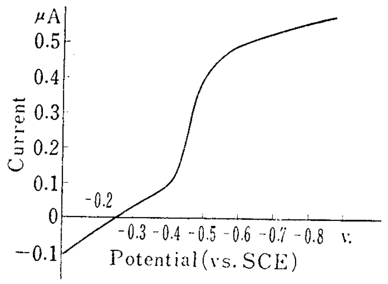

Fig. 6. Current–Potential Curves (25°±0.2°) Recorded wave

cell resistance : $1.51\times10^4\,\Omega$
concentration : $6.453\times10^{-5}\,M/L$

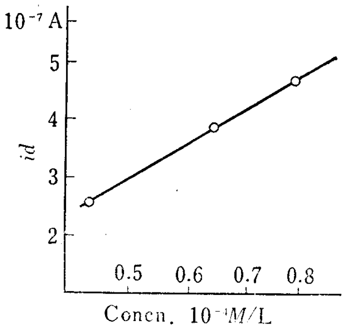

Fig. 7. Calibration Curve for 6,13-Pentacenequinone (25°±0.2°)

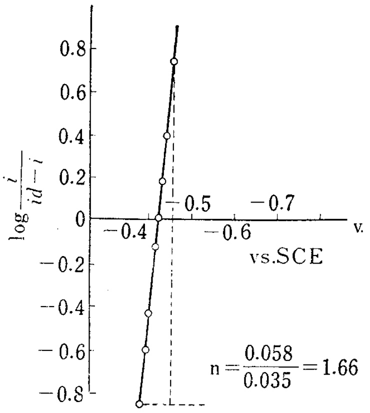

Fig. 8. Log i/i_d-i—Voltage

case of (Ⅱ), were obtained as −0.447 v. vs. SCE and 2.830 as the mean value of those given in Table Ⅲ. The linear relationship between concentration and i_d is shown in Fig. 7. The log i/i_d-i is plotted in Fig. 8, whose slope is 1.66, showing two-electron exchange per molecule in the polarographic reduction.

Discussion

Half-wave potentials of *p*-quinones reported previously1) and of (I), (Ⅱ), and (Ⅲ) are summarized in Table Ⅳ. From this table, the ease with which they are reduced at the dropping mercury electrode is in the descending order of *p*-benzoquinone, *p*-naphthoquinone, 1,4-anthraquinone, 9,10-anthraquinone, 5,12-naphthacenequinone, and 6,13-pentacenequinone (A).

In the case of polycyclic *p*-quinones with four or five fused benzene rings, the ease with which they are reduced is in the descending order of dibenz[*a,h*]anthracene-7,14-quinone, benz[*a*]anthracene-7,12-quinone, 5,12-naphthacenequinone, and 6,13-pentacenequinone (B), since $E_{1/2}$1) of benz[*a*]anthracene-7,12-quinone and dibenz[*a,h*]anthracene-7,14-qninone is −0.168 and −0.137 v. vs. SCE, respectively.

Table Ⅳ.

Substance	$E_{1/2}$ (vs. SCE) (v.)	Substance	$E_{1/2}$ (vs. SCE) (v.)
p-Benzoquinone (*p*-BQ)	+0.338	9,10-Anthraquinone (9,10-AQ)	−0.240
1,4-Naphthoquinone (*p*-NQ)	+0.105	5,12-Naphthacenequinone (NaQ)	−0.345
1,4-Anthraquinone (1,4-AQ)	+0.027	6,13-Pentacenequinone (PQ)	−0.447

Table Ⅴ.

	p-BQ	*p*-NQ	1,4-AQ	9,10-AQ	5,12-NaQ	6,13-PQ
Hydroquinone anion	2	3	4	4	5	6
Quinone	1	2	3	4	6	9
Ratio $\left(\frac{\text{hydroquinone}}{\text{quinone}}\right)$	2	1.5	1.33	1	0.83	0.66

In the case of linear aromatic *p*-quinones, the order shown in the sequence (A) should also agree with the order in which the ratio of *p*-hydroquinone anion to *p*-quinone decreases in the number of principal limiting structures, as discussed in detail in a previous paper.1) This agreement is illustrated in Table Ⅴ. In the (B) sequence, it is interesting to note that angular *p*-quinones, whose corresponding hydrocarbons are carcinogens, are reduced more easily than the corresponding linear *p*-quinones.

The author expresses his deep gratitude to Prof. Morizo Ishidate, the late Dr. Takashi Isshiki, and Dr. Keizo Tada for their continued and kind guidance throughout the course of this study. He is indebted to Dr. Eisaku Kimura for his technical help.

Summary

The half-wave potential ($E_{1/2}$) and diffusion current constant (I_D) of three linear aromatic *p*-quinones, 1,4-anthraquinone (I), 5,12-naphthacenequinone (II), and 6,13-pentacenequinone (III), were measured under identical conditions by the nonaqueous polarography in glacial acetic acid containing 0.25*N* ammonium acetate. The half-wave potential of (I), (II), and (III) was +0.027 v., −0.345 v., and −0.447 v. vs. SCE, respectively. The ease with which they are reduced at the dropping mercury electrode is in the descending order of 1,4-anthraquinone, 5,12-naphthoanthraquinone, and 6,13-pentacenequinone. This order agrees with the resonance theory as in the case of quinones described in previous papers.

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81. Tomoharu Okuda, Yasuhiro Takanashi, and Masao Tsuruoka : Studies on the Streptomyces Antibiotic, Cycloheximide. XII.[1] N-Mercuricycloheximides.

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Cycloheximide is an antiyeast antibiotic produced by *Streptomyces griseus* and others, and its isolation from the fermentation broth is carried out by solvent extraction, absorption on activated carbon, or by ion exchanger technique. As expected from its molecular formula (I), cycloheximide can form a salt or a chelate compound with a metal ion, in which an imide hydrogen or β-hydroxy-ketone moiety takes a part. If such metal ions are found, they would be useful in isolating cycloheximide from its fermentation beer selectively.

The present paper is on the selection of metal ions for the above purpose and also with the preparation and structure of the inorganic or organic mercury compounds of cycloheximide which were successfully obtained as pure crystals. Briefly mention is also made on the antifungal activity and rodent reppellency of N-phenylmercuricycloheximide.

Selection of Metal Ions to Form Water-insoluble Compound of Cycloheximide

To a solution of one of the metal salts given in Table I, 0.5% aqueous solution of cycloheximide was added and, in case where no precipitation was observed, a solution of sodium acetate and dilute ammonium hydroxide solution were added successively to the above solution, and the appearance of precipitation was observed.

Among the metal ions examined, mercury(II) ion gave a desired insoluble precipitate in neutral or slightly acid condition. Copper(II) and cobalt(III) ions respectively gave insoluble purple and blue precipitates in the presence of ammonium hydroxide. The same copper(II) compound was also obtained by the addition of tetraamminecopper(II) sulfate

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[*1] Toda-machi, Kita-adachi-gun, Saitama-ken (奥田朝晴, 高梨保博, 鶴岡正夫).

1) Part XI. M. Suzuki : This Bulletin, 8, 778 (1960).