63. **Keizo Tada** : Nonaqueous Polarography of Quinones. III*. Polarography of 1,2,5,6-Dibenzanthraquinone(9,10) in Glacial Acetic Acid.

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This experiment was carried out as one of the series of studies on the nonaqueous polarography of quinones, in relation to researches for carcinogens.

Since glacial acetic acid was found to be a favorable solvent for the polarography of less soluble quinones, it was presumed that the polarography of the subject quinone (I) also might be carried out satisfactorily using this solvent.

In order to compare the results being obtained in this experiment with those obtained in previous two experiments[1,2], all the measurements were carried out in strictly the same conditions as those in the previous cases.

The polarogram of (I) in glacial acetic acid containing ammonium acetate was satisfactorily obtained, although the slope of the wave recorded in each run widely differed with each other and from that of the real wave, owing to large IR drop, and the correction was necessary in each run as described in the previous paper.

In Fig. 1, the recorded polarogram of (I) is shown in broken line, the corresponding polarogram corrected for IR drop in each run in solid line, and blank polarogram in chain line.

It was found that (I) produced a well-defined single wave and it exhibited a half-wave potential at -0.137 V vs. S.C.E., which was 0.031 V positive than that of 1,2-benzanthraquinone(9,10) (II).

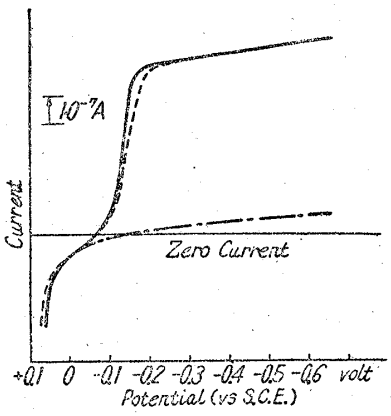

Fig. 1.
Current-Potential Curves
(25°±0.2°)
Broken line : Recorded wave
(Cell resistance=$3.4\times10^4\Omega$)
Solid line : Corrected wave for IR drop
Chain line : Residual current

Table I.

C $\times10^{-4}$ M	i_d $\times10^{-7}$A	$i_d/cm^{2/3}t^{1/6}$
0.60_0	1.67_6	2.36_3
1.07_5	2.97_0	2.38_2
1.80_1	5.12_9	2.40_6
2.49_6	7.37_3	2.51_1
3.22_6	9.47_5	2.48_0
	mean value	2.42_6

All of diffusion currents were measured easily under various concentrations and they are given in Table I. The plotting of these against concentrations illustrated a linear relationship as shown in Fig. 2. The diffusion current constant, 2.42_6, was obtained as the mean value of these given in Table I and they were well coincident with minimum errors as shown in Fig. 2.

By plotting the $\log i/i_d-i$ against various voltages over the corrected wave, a linear relationship was obtained as shown in Fig. 3, whose slope, 2.07, indicated the polarographic reduction of (I) in this medium was a typical reversible reaction involving two-electron change per molecule as were the cases for (II) and anthraquinone (III).

* Isshiki Takashi : Nonaqueous Polarography. III.
** Hongo, Tokyo (多田敬三).
1) Takashi Isshiki, Keizo Tada : This Bulletin, **2**, 266 (1954).
2) Keizo Tada : *Ibid.*, **2**, 270 (1954).

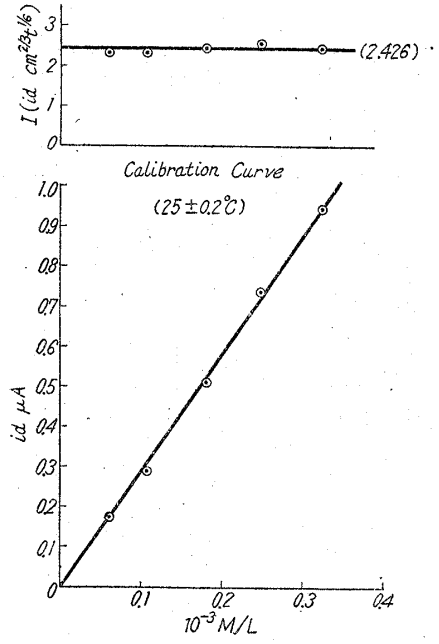

Fig. 2.

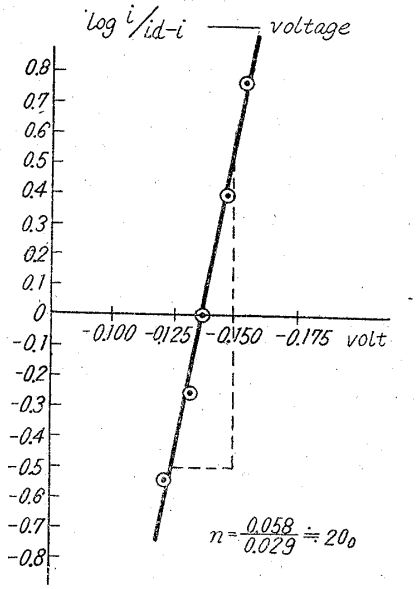

Fig. 3.

Discussion

Fieser[3], already in 1931, measured normal reduction-oxidation potentials (ε) of various polycyclic aromatic quinones involving those mentioned above by electrochemical titration in 90% ethanol with some chemical oxidizing agents.

These values have been believed to be reliable and have still played an important part in many fields. On the other hand, however, polarographic methods have scarcely appeared in the electrochemical field for these quinones because of their insolubilitiy and it might be able to check Fieser's values using polarography.

Now, from the series of our studies, $E_{1/2}$'s have been obtained under same conditions, though only for three quinones as shown in Table II, the results obtained in these works together with their normal potentials measured by Fieser are summerized.

Table II.

	$E_{1/2}$ (V)*	ε (V)**	$\varepsilon - E_{1/2}$	I
Anthraquinone	-0.24_0	0.15_6	0.39_6	3.18_6
1,2-Benzanthraquinone	-0.16_8	0.22_8	0.39_6	2.50_7
1,2,5,6-dibenzanthraquinone	-0.13_7	0.25_7	0.39_4	2.42_6

* vs. S. C. E. corrected for IR drop.
** vs. hydrogen electrode measured by Fieser.

Comparing these half-wave potentials with normal potentials (ε), it was found that differences between $E_{1/2}$ and ε regarding (I), (II), and (III) were 0.394, 0.396, and 0.396 V, respectively. Difference between $E_{1/2}$'s for (I) and (II) was 0.072 V and that for (II) and (III) was 0.031 V and they were well coincident with those obtained from the same comparison between normal potentials, 0.072 V and 0.029 V, respectively. This indicates, if Fieser's values were not wrong, the results obtained from these works would also be reliable.

Regarding the diffusion current constants (I_D) of these quinones (Table II), having analogous skeleton in their structures, the following equation can approximately be used in such case that they are measured at the same temperature and in the same medium.

3) L. F. Fieser: J. Am. Chem. Soc., **53**, 1128 (1931).

$$I_D = KM^{-1/6}$$

where M represents molecular weight, and K, the constant calculated from fluid dynamics.

The values for three quinones were found to follow the above equation closely, though that of (III) seems to be too large.

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Experimental

Reagents—1,2,5,6-Dibenzanthraquinone(9, 10) was synthesized[4] by oxidation of 1,2,5,6-dibenzanthracene (264~266°) supplied from Eastman Kodak Co., purified by passing its *o*-dichlorobezene solution through activated alumina column, and finally recrystallized from xylene. Other reagents, apparatus, and procedures were all same as described in the previous paper[1] and all measurements were carried out at 25°±0.2°.

Besides these points, no special comment is required except that this quinone was less soluble than the previous quinones in this medium, though no difficulties were encountered during the experiment.

Summary

The polarography of 1,2,5,6-dibenzanthraquinone could be favorably carried out in glacial acetic acid containing ammonium acetate as done in the previous cases. The half-wave potential(−0.137 V vs. S.C.E.) and the diffusion current constant (2.42_6) was obtained with minimum errors in each case. A typical reversible reaction involving the two-electron change was illustrated.

Some discussions were made in relation to the values of $E_{1/2}$ and I_D for the three quinones hitherto obtained by this method in our laboratory.

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4) J. W. Cook : J. Chem. Soc., **1933**, 1957.