Procedure—The solution was brought to 25°±0.2° by immersing in a constant temperature bath and made free from oxygen with hydrogen saturated with the solvent for 10~15 minutes. Then current-voltage relationship was plotted or recorded.

Drawing—$E_{1/2}$ and i_d were determined on each polarogram according to the drawing shown in Fig. 1, curve 5.

In this figure, the straight line ($\overline{ab}$) parallel to the gently sloping residual current ($\overline{cd}$), was drawn through the starting point (e) of the more steep diffusion current plateau.

Summary

Half wave potentials and diffusion current constants of *p*-aminomethylphenyl isopentyl ketone at various pH were determined. They are summarized in the accompanying Tables. The electrons per molecule, namely two, contributing for the polarographic reduction of the ketone in neutral medium were also calculated from the decrease of diffusion current after the prolonged electrolytic reduction at the dropping mercury electrode.

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58. **Takashi Isshiki, Yasushi Mashiko, and Mioko Ninomiya** : On the Polarography of 2-Acetamido-5-nitrothiazole.

(*Pharmaceutical Institute, Medical Faculty, University of Tokyo**)

Though a few procedures have been applied to the reduction of 5-nitro derivatives of thiazoles, no fruitful result has been obtained up to date[1].

Owing to the +M effect of the nuclear sulfur atom, thiazole is very stable to reducing reactions and no polarographic wave was obtained for 2-acetamidothiazole (below pH 9.65). It was, however, found that 5-nitro derivative of this compound was reducible at the dropping mercury electrode and this really gave distinct polarographic waves.

In basic solution where the solvent was composed of equal volumes of buffer solution (pH 9.65) and isopropanol, tylose was added to make 0.025% concentration. One pre-step was recorded before the main wave was developed. Similar phenomenon was also observed with the cell solution, where only pH of aqueous buffer solution (pH 7.85), differed from that mentioned.

Finally, the typical one-step wave as shown in Fig. 1 was obtained when equal volumes of buffer solution (pH 3.08) and isopropanolic solution of the nitro compound were mixed to form the cell solution containing 0.025% of tylose, as the maximum surpressor.

Half-wave potential in this cell solution is −0.32 V vs. S.C.E. The diffusion current is a linear function of the molar concentration of the compound as shown in Fig. 2. The value of diffusion current constant $i_d/\mathrm{c}m^{2/3}t^{1/6}$ in each concentration is also given in Fig. 2. The diffusion current constant as the mean value was calculated from these data and was found to be 4.11_1.

The number of electrons contributing for the polarographic reduction can be calculated from the following Gilbert-Rideal's equation[2],

$$n=\frac{-1}{2.303\times F\times v}\times\frac{i_d}{c}\times\frac{dt}{d(\log h)}$$

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* Hongo, Tokyo (一色 孝, 益子 安, 二宮美保子).

[1] e. g., Ochiai, Nagasawa : J. Pharm. Soc. Japan, **58**, 1048 (1938).

[2] Gilbert, Rideal : Trans. Farad. Soc., **1951**, 396.

where the meaning of letters are the same as those previously reported³⁾.

In Fig. 3 the logarithm of the wave-height measured in arbitrary terms from the polarographic record made in intervals was plotted against the time for electrolysis.

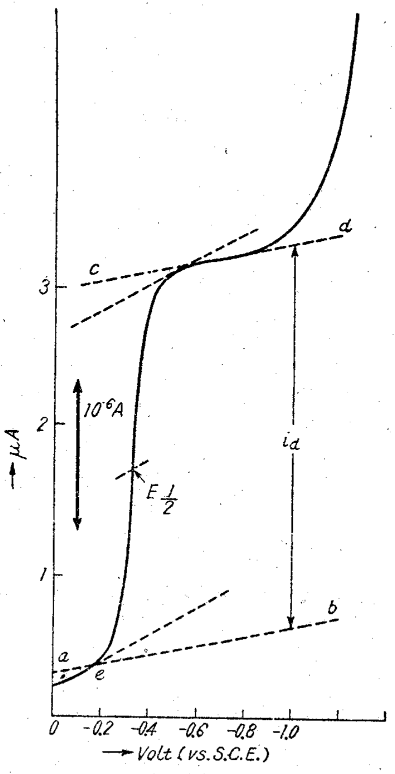


Fig. 1. Current-Voltage Curve at pH 3.08 Concentration: $5\times10^{-4}M$/L.

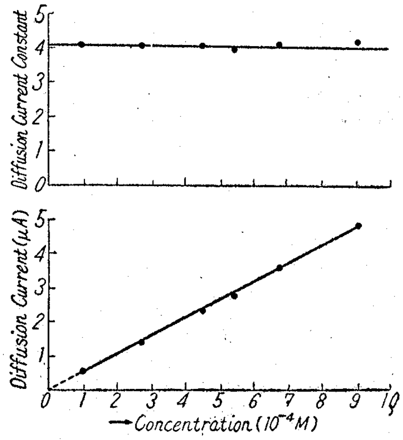


Fig. 2. Diffusion Current and Diffusion Current Constant at various Concentrations

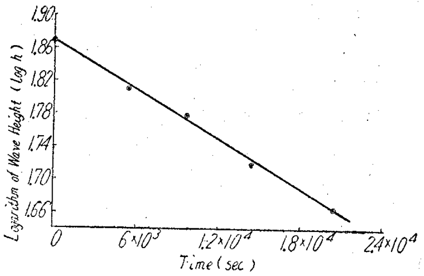


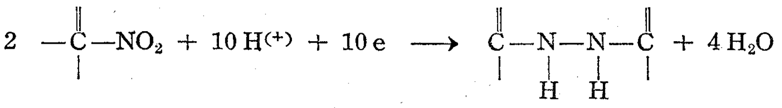
Fig. 3. Electrolytic Reduction at the Dropping Mercury Electrode (Applied Voltage : −0.8 V)

TABLE I.

C	i_d	v	$d(\log h)/dt$	n
$5.34\times10^{-4}M$	2.59×10^{-6}A	4.45×10^{-4}L.	-1.01×10^{-5}	4.9

The value of $d(\log h)/dt$ which corresponds to the tangent of the slope in Fig. 2 and the rest of the data required for the evaluation of n are summarized in Table I.

The result shows that five electrons per molecule are involved in the polarographic reduction of the nitro compound. To account for this result, it may be presumed that five hydrogen atoms per molecule are also taken into the reaction and that the dimerization occurs with the formation of hydrazine derivative.



$$2\ -\overset{\|}{\underset{|}{C}}-NO_2 + 10\,H^{(+)} + 10\,e \longrightarrow \overset{\|}{\underset{|}{C}}-\underset{H}{\underset{|}{N}}-\underset{H}{\underset{|}{N}}-\overset{\|}{\underset{|}{C}} + 4\,H_2O$$

This is not always in accord with the results obtained by many investigators⁴⁾ on the

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3) Isshiki, Kajima, Noguchi : This Bulletin **2**, 253 (1954).

4) Kolthoff, Lingane : "Polarography," Interscience Publishers, Inc., New York, 746∼778 (1952).

polarographic reductions of nitro compounds (2, 4, or 6 electrons per molecule). In this connection another mechanism involving simultaneous formation of both amino and hydroxylamino derivatives in equal amounts may also be considered in our case.

On the other hand, when the number of electrons involved in the reduction are many, the experimental errors accompanying the prolonged electrolysis cannot be neglected, because they might have influence upon the result of the calculation. Further examination will, therefore, be in need for the accurate determination of the reduction mechanism of 2-acetamido-5-nitrothiazole.

The authors wish to express their appreciation to Prof. Ishidate for his direction and advice. They also wish to thank Mr. Tada and Dr. Yamamoto for kind assistance.

Experimental

Apparatus—Current-voltage curves were recorded using Yanagimoto Polarograph improved in our laboratory. Sensitivity of galvanometer ($3.42_0 \times 10^{-9}$ A/mm. at the maximum sensitivity) was same as the one previously reported[3]. Calibration of polarograph was also made. Half-wave potentials (vs. S. C. E.) were obtained by using our H-type electrolysis cells[3]. No correction was made for IR-drop or junction potentials.

Wave-heights were determined using both H-type cells[*] and ordinary cells having an internal mercury pool. Measurements were carried out at 25° ± 0.2°. At a mercury level of 514 mm. the capillary was characterized as follows: m (mg./sec., in distd. water) 1.02_2, t (sec./drop, in the cell solution at −0.32 V vs. S. C. E.) 3.67; $m^{2/3} t^{1/6}$ 1.26_0.

Reagents—2-Acetamido-5-nitrothiazole was prepared by Dr. Yamamoto according to his report[5].

Buffer Solution—Clark-Lubs' buffer solution of pH 3.08 was used and value was determined using Towa-Dempa glass electrode pH meter.

Cell Solution—The weighed nitro compound was dissolved in the definite quantity of pure isopropanol, then, the same volume of buffer solution (pH 3.08) containing 0.05% of tylose was added. Heating must be avoided for the final cell solutions. The mol. ratio of the nitro compound and the total supporting electrolytes in the final cell solution was about 1 : 30 at the highest concentration of the electrolytically active substance which was investigated. Addition of potassium chloride to the cell solution up to 0.2 M/L., gave practically no effect to the height of the waves. No measurement of pH was made for these final cell solutions.

Procedure—The procedure was same as that of previous report[3].

Drawing—$E_{1/2}$ and i_d were determined on each polarogram according to the drawing as shown in Fig. 1. In this figure, the straight line (ab) parallel to the gently sloping diffusion current plateau (cd), was drawn through the end point (e) of more steep residual current slope.

Summary

Half-wave potential (−0.32 V vs. S.C.E.) and diffusion current constant (4.11_1) were determined in the equal volume mixture of buffer solution (pH 3.08) and isopropanol containing 0.025% of tylose as a whole.

It was also calculated from Gilbert-Rideal's equation that five electrons per molecule were taken into the reduction. In this connection, the reaction mechanisms were discussed and the results were criticized.

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[*] cf. Fig. 4, this Bulletin, **2**, 268 (1954).

[5] Yamamoto: J. Pharm. Soc. Japan, **72**, 1017 (1952).