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The Polarographic Behavior of Aliphatic Aldehydes in Buffer Solutions Containing *o*-Phenylenediamine

Tamotsu WASA and Sôichirô MUSHA

Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Sakai

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Formaldehyde (I), acetaldehyde (II), propionaldehyde (III), *n*-butyraldehyde (IV), *n*-caproaldehyde (V), and *n*-octaldehyde (VI) condense with *o*-phenylenediamine (OPD) to yield products, each of which gives a single, irreversible but well-defined oxidation wave ($E_{1/2}$ *vs.* SCE at pH 8.0: −0.240 V for I, −0.242 V for II, −0.263 V for III, −0.290 V for IV, −0.316 V for V, and −0.338 V for VI). From these findings, it has been deduced that the condensation products of aldehydes with OPD would be benzimidazoline derivatives, which would be oxidized to benzimidazole derivatives at the dropping mercury electrode. Linear relations between the limiting currents of the condensation products with OPD and the concentrations of aldehydes [$(1—20)\times10^{-4}$ M], except for I, were obtained under the following conditions: pH, 6—8 ($\mathrm{pH}_{i\,max}$); the concentration of OPD, 2×10^{-2} M; the temperature, 25°C; and the condensation time, 15—60 min. The method was then applied practically in the determination of the purity of a commercial product of II and the quantity of II in the presence of glyoxal.

It has well been known that most aliphatic aldehydes show single reduction waves at the dropping mercury electrode in neutral and alkaline solutions containing lithium or tetraalkylammonium salt as the supporting electrolyte in the range of voltage between −1.6 V and −1.8 V *vs.* SCE, and that these waves can be used in the determination of aliphatic aldehydes.[1-4] However, the limiting current is markedly influenced by the pH and the temperature of the electrolytic solution,[5,6] and also decreases with time in the alkaline region because of the instability of these aldehydes.[7] For analytical use, in order to obtain the wave height proportional to the aldehyde concentration, the experimental conditions must be strictly controlled. To avoid this shortcoming, indirect polarographic methods which involve the chemical reactions of aldehyde with carbonyl reagents have been reported.[8-10]

The authors have previously reported on the oxidation waves of the condensation products of hydroxyaldehydes with *o*-phenylenediamine (OPD) in various buffer solutions, and on the polarographic determination of glycolaldehyde and glyceraldehyde.[11]

The present paper will describe the polarographic behavior of aliphatic aldehydes, *i. e.*, formaldehyde (I), acetaldehyde (II), propionaldehyde (III), *n*-butyraldehyde (IV), *n*-caproaldehyde (V), and *n*-octaldehyde (VI), in various buffer solutions containing an excess of OPD, and will present a method for determining such aldehydes by using this oxidation wave.

Experimental

Formaldehyde was a commercial product (Formalin, about 37%) from Wako Pure Chemical Industries, Ltd.; it was used without further purification. II was prepared from paraldehyde by distillation in the presence of a 1 vol% of concentrated sulfuric acid.[12] All the other aldehydes (III, IV, V, and VI) used were purified by the distillation of their commercial products. Aqueous or ethanolic stock solutions of the aldehydes were prepared at about 10^{-2} M; these concentrations were checked by the titration method.[13] All the other chemicals were the same as those used in previous

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works.[11,14,15] As for the buffer solutions, Britton-Robinson buffers (BR) were mainly employed except for examining the effect of the components of the buffer solution. No maximum suppressor was added, since no maximum was observed under the present polarographic conditions.

The apparatus and the experimental procedures were the same as those reported in previous papers.[11,14,15] To minimize the loss of aldehydes, the dissolved oxygen was removed by bubbling nitrogen which had previously been passed through a solution of the same composition. Reference electrode: SCE. Characteristics of capillary: m=1.143 mg/sec, t=4.00 sec/drop in the buffer solution at 0 V *vs.* SCE. The accuracy of the temperature control was ±0.1°C.

Results and Discussion

Oxidation Waves of the Condensation Products of Aliphatic Aldehydes with OPD. All the aliphatic aldehydes (I—VI) examined show an ill-defined and unstable reduction wave in alkaline media, as may be seen in Fig. 1(a). In buffer solution containing an excess of OPD, however, they give a well-defined oxidation wave (Fig. 1(b)) corresponding to the condensation products, which are probably benzimidazoline derivatives, as has been previously reported for hydroxyaldehydes.[11]

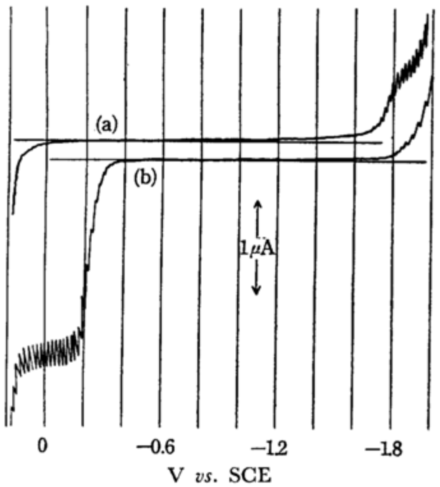

Fig. 1. Polarograms of acetaldehyde with or without OPD at 25°C.

(a) 2×10^{-3} M II in BR buffer (pH, 8.0)
(b) 6.5×10^{-4} M II in BR buffer (pH, 8.0) containing 2×10^{-2} M OPD; Condensation: 60 min

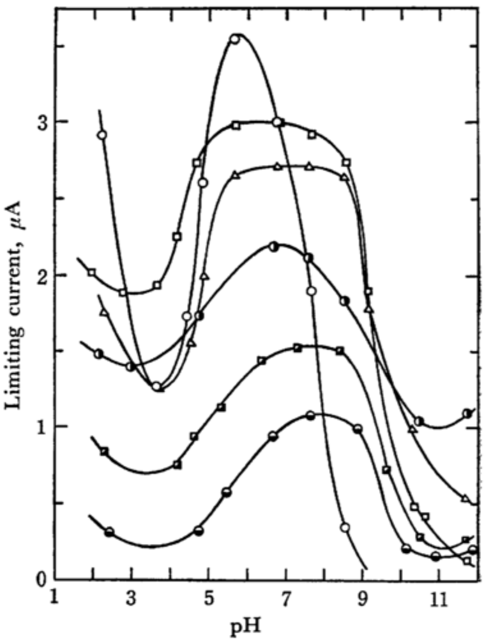

Fig. 2. Effect of pH on the oxidation waves of the aldehydes (1×10^{-3} M) in BR buffer containing 2×10^{-2} M OPD at 25°C.
Condensation: 60 min; ○—I, □—II, △—III, ◑—IV, ◪—V, and ◒—VI

The Effect of pH. When the concentrations of aldehydes and OPD were kept constant and when polarograms were recorded 60 min after the addition of OPD at 25°C, the relationships between the limiting currents of the condensation products and the pH were as shown in Fig. 2. All the aldehydes examined, with the exception of I, exhibit almost the same polarographic behavior: the limiting currents reach their maximum values in the pH range between 6 and 8 and then decrease beyond this pH region. It seems that the decrease in the height of the oxidation waves with an increase in the pH on the alkaline side is related to the decrease in the rate of the condensation reaction, while the other decrease, on the acidic side, is due to some conversion of OPD involving protonation and also to the instability of the condensation products. The limiting current for I, with an increase in the pH, reaches its maximum value at a pH value of about 5.8; then it decreases markedly with a further increase in the pH, while, at the same time, the electrolytic solution becomes turbid. The optimum pH ranges, $\mathrm{pH}_{i\ max}$, in which the oxidation wave corresponding to each of the aldehydes shows its maximum value, are presented in Table 1, together with the equilibrium constants (K'). At the $\mathrm{pH}_{i\ max}$ the reaction of aldehyde with OPD reached its equilibrium state within 5—10 min after the addition of OPD and the condensation products were comparatively stable. The oxidation wave of the condensation products was diffusion-controlled; there is a proportionality between the limiting currents and the square root of the heights of mercury reservoir.

The changes in the half-wave potentials with the

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TABLE 1. OPTIMUM pH (pH$_{i\,max}$) AND EQUILIBRIUM CONSTANT (K') FOR THE CONDENSATION REACTION
Aldehyde: 1×10^{-3} M, OPD: 2×10^{-2} M; Condensation: 60 min, 25°C, BR buffer

Aldehyde	I	II	III	IV	V	VI
pH$_{i\,max}$	5.8	5.5—8	6—8	6—7.5	6.5—8.5	7—9
K', l/mol	474	176	138	117	73	60

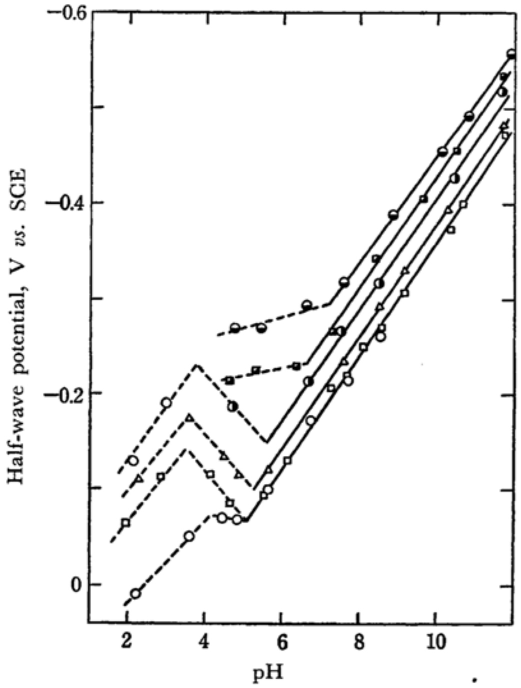


Fig. 3. pH-dependence of the half-wave potentials at 25°C.
Aldehyde: 1×10^{-3} M, OPD: 2×10^{-2} M; Condensation: 60 min, BR buffer; ○—I, □—II, △—III, ◑—IV, ◩—V, and ◒—VI

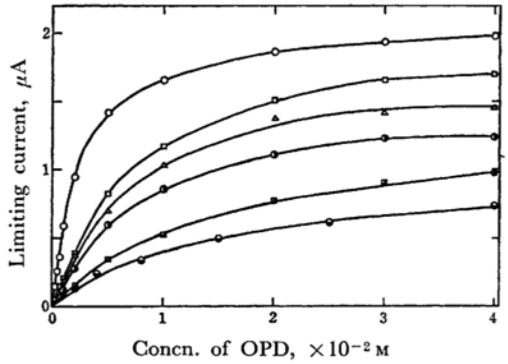
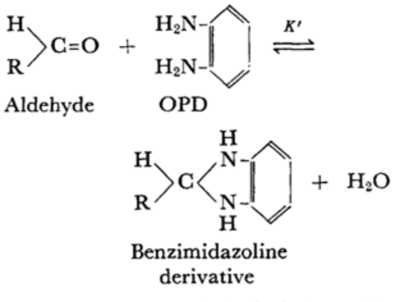


Fig. 4. Relationship between the limiting currents and the concentrations of OPD at 25°C.
Aldehyde: 5×10^{-4} M; Condensation: 60 min in BR buffer with pH$_{i\,max}$; ○—I, □—II, △—III, ◑—IV, ◩—V, and ◒—VI

pH value are shown in Fig. 3. At pH values higher than pH$_{i\,max}$, the half-wave potential of the oxidation wave corresponding to each aldehyde showed a linear relation with the pH value (inclination; −60 mV/pH); this relation shifted to a more negative potential with an increase in the number of carbon atoms in the aldehydes used. At pH values of 4—6, it was also observed that the wave became less steep and that the half-wave potential shifted discontinuously.

The Effect of Concentration of OPD. The relationships between the limiting currents of the condensation products measured 60 min after the addition of OPD at 25°C and the concentration of OPD are shown in Fig. 4, when the concentration of aldehydes was kept constant at the pH$_{i\,max}$ value corresponding to each of the aldehydes. From the data of Fig. 4 and the fact the half-wave potential shifts to a more negative potential with an increase in the concentration of OPD, it may be deduced that the condensation reaction attains an equilibrium state.[11] The reaction may be written as follows:

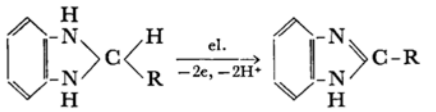


(1)

$R=C_nH_{2n+1}$; $n=0$, 1, 2, 3, 5, and 7

The equilibrium constants obtained in a manner similar to that previously reported for glyceraldehyde[11] are given in Table 1. Since the equilibrium constants for all the aldehydes are relatively small, for analytical purposes the concentration of OPD in the reaction mixture should be kept in a large excess and should be kept constant.

From the facts that no a. c. polarogram was obtained, except for a small peak which seems to be due to the adsorption, and that no reduction wave was obtained with the oxidation product by means of a controlled-potential electrolysis, the electrode reaction of the condensation products may be concluded to be an irreversible one. Moreover, because the UV-absorption spectra of the electro-oxidation products were in accordance with that of benzimidazole, the electrode process may be expressed as follows:



(2)

The discontinuous change in the half-wave potentials at pH values between 4 and 6, as seen in Fig. 3, seems to be due to the change in the electrode process resulting from the protonation of benzimidazoline derivatives.

The Effect of Bubbling Nitrogen. As a result of the volatility of all the aliphatic aldehydes examined, we desired to ascertain the effect of the deoxygenating time on the constancy of the wave heights of the condensation products by bubbling nitrogen. For that reason, a series of measurements were conducted to check the possible effects due to different bubbling times; the results obtained are summarized in Table 2. No remarkable decrease resulting from the volatility of aldehydes by bubbling nitrogen was observed when a large excess of OPD was present in the reaction mixture. However, a discrepancy apparently due to the oxidation of the condensation product by dissolving oxygen was observed. For analytical purposes, therefore, it is necessary to remove the dissolving oxygen by bubbling nitrogen immediately after the preparation of the electrolytic solution.

TABLE 2. INFLUENCE OF BUBBLING NITROGEN ON THE LIMITING CURRENT OF THE CONDENSATION PRODUCT

Acetaldehyde: *ca.* 1.5×10^{-3} M; Condensation: 2×10^{-2} M OPD, 60 min, 25°C, pH 8.2

Time, min		5	10	15	20	30
i, μA	early stage	4.62	4.62	4.58	4.71	4.65
	final stage	4.08	4.14	4.16	4.28	4.35

The Effect of the Temperature. The time required for the condensation shortened upon a rise in the temperature, but at temperatures higher than 30°C it was also observed that the anodic limting current, after attaining its maximum value, decreased with the time. The changes in the wave heights of the condensation products with the temperature at a pH value of 7.5 are shown in Fig. 5. The smaller temperature coefficients than those observed for the diffusion-controlled currents may indicate that the equilibrium of Eq. (1) is shifted more in the dissociation direction with the temperature.

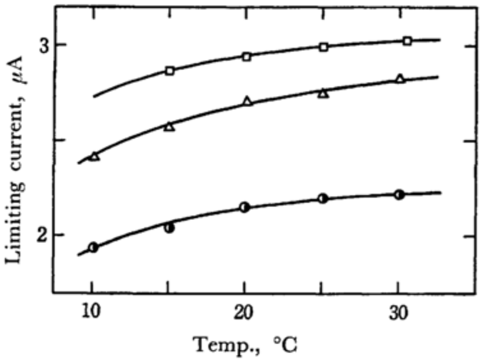


Fig. 5. Effect of the temperature on the limiting currents of the condensation products.
Aldehyde: *ca.* 1×10^{-3} M; Condensation: 2×10^{-2} M OPD, BR buffer (pH, 7.5), 2% ethanol; □—II, △—III, and ◑—IV

Application to the Determination of Aliphatic Aldehyde. On the basis of the experimental facts described above, the following conditions can be recommended for the determination of aliphatic aldehydes by using the oxidation wave of the condensation products with OPD: $\mathrm{pH}_{i\ max}$ for pH, 2×10^{-2} M for the concentration of OPD, 25°C for the temperature, and 15—60 min for the condensation time. These recommended conditions are almost the same as those recommended for hydroxyaldehydes in a previous paper.[11] To obtain a better reproducibility, the dissolving oxygen must be removed by bubbling nitrogen for 10 min as soon as possible after the preparation of the electrolytic solution because of the oxidizable property of the condensation product. Under these conditions, linear relations are obtained between the concentrations of all the aldehydes except for

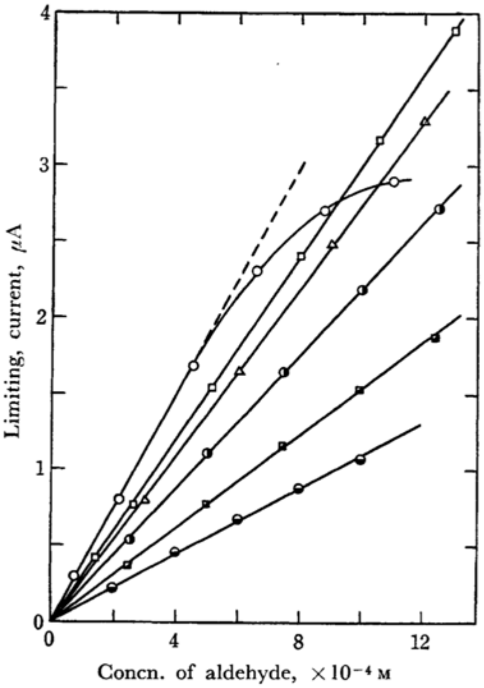


Fig. 6. Relation between the limiting currents of the condensation products and the concentrations of aldehydes in BR buffer at 25°C.
Condensation: 2×10^{-2} M OPD, 30 min; ○—I, □—II, △—III, ◑—IV, ◪—V, and ◒—VI.

I and the limiting currents of their condensation products in the range of $(1\text{—}20)\times10^{-4}$ M, as Fig. 6 shows.

The purity of a commercial aqueous solution (about 80%) of II was determined by means of the standard addition method[11] after the proper preliminary dilution of the sample with distilled water free from oxygen, utilizing the optimum conditions previously specified. The results obtained are shown in Table 3, along with those obtained by a modification of Siggia's method.[16] The results obtained by the two methods are in good agreement with each other.

The determination of II in an artificial sample containing II and glyoxal was also carried out; the results of this analysis are listed in Table 4. The presence of glyoxal does not seriously interfere with the determination of II by the polarographic OPD method, but it interferes strongly with the determination of II by the titration method.

The presence of alcohols, carboxylic acids, and esters in the sample does not interfere with the determination of any of the aldehydes examined, since these substances do not show the oxidation wave under the present experimental conditions. Though acetone does show an anodic wave under the present experimental conditions, it does not cause any interference at concentrations of less than 3×10^{-2} M. Sulfite ion strongly interfered with the determination of aliphatic aldehydes. Since the condensation products of all the aliphatic aldehydes and hydroxyaldehydes[11] with OPD behave similarly at the dropping mercury electrode, these aldehydes interfere with the determination of one other.

TABLE 3. RESULTS OF THE DETERMINATION OF ACETALDEHYDE IN COMMERCIAL PRODUCT

Condensation: 2×10^{-2} M OPD, 25°C, 60 min in BR buffer (pH 8.0)

Exp. No.	Acetaldehyde contents, %	
	Polarographic	Titrimetric*
1	75.5	75.2
2	75.9	76.0
3	75.3	76.0
4	75.6	75.7
5	76.7	76.5
Average	75.8_0	75.8_8

* The modified Siggia's method[16]

TABLE 4. ANALYSIS OF ACETALDEHYDE IN AQUEOUS SOLUTION CONTAINING ACETALDEHYDE AND GLYOXAL

Condensation: 2×10^{-2} M OPD, 25°C, 60 min BR buffer (pH 8.0)

Concn. of carbonyl compds., M		Acetaldehyde found M	
Acetaldehyde	Glyoxal	Polarographic	Titrimetric*
0.134_6	—	0.133	0.134
—	0.0420_8	0	0.0686
0.134_6	0.0420_8	0.135	0.207
0.0269_1	0.0420_8	0.0264	0.101
0.0672_8	0.0841_6	0.0673	0.214
0.0672_8	0.00841_6	0.0668	0.0783

* The modified Siggia's method[16]

The present polarographic method is particularly well suited for the determination of aliphatic aldehydes in the presence of some other compounds which are polarographically reducible and not distinguishable by using reduction waves.

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16) Sidney Siggia and W. Maxcy, *Ind. Eng. Chem., Anal. Ed.*, **19**, 1023 (1947).