[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY OF POLAROID CORPORATION]

Polarographic Studies on Aliphatic Polyene Aldehydes

By MELVIN FIELDS AND ELKAN R. BLOUT

The polarographic behavior of polyene aldehydes is of interest in connection with other research in progress in this Laboratory.[1,2] Several investigators have studied the polarographic behavior of compounds containing one or two aliphatic carbon–carbon double bonds conjugated with a carbonyl group,[3,4,5] but polarographic data for the more highly unsaturated ketones or aldehydes have not been reported.

In this paper we are reporting the results of work on the behavior at the dropping mercury electrode of unsaturated aldehydes of the type I

$$CH_3—(CH=CH)_x—CHO \qquad I$$
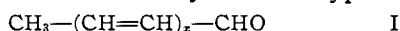
where x equals 1, 2, 3, 4 and 5. We were particularly interested in determining the effect of increasing chain length on the number, relative heights and half-wave potentials of the polarographic waves. In addition, we have studied the effect of pH on the polarographic characteristics of each compound. We have also calculated from the Ilkovic equation the diffusion coefficients of these polyenic aldehydes.

Experimental

Preparation of Aliphatic Polyene Aldehydes.—These compounds were prepared and purified by the procedures described or referred to in a previous paper.[1] The samples used for the polarographic measurements were of the same purity as those used for spectral measurements.

Instrument and Cells.—Polarographic measurements were made using a simple manual apparatus similar to the one described by Lingane and Kolthoff.[6] The usual H-type polarographic cell with a saturated calomel reference electrode was used. At a pressure of 65.0 cm. the capillary had a drop time of 3.5 seconds and an m-value of 1.908 mg. of mercury per second measured on open circuit in 50% aqueous dioxane solution tenth molar in potassium chloride.

Buffers.—The compositions of the stock buffer solutions which were prepared are listed below; when diluted with an equal volume of water or of dioxane they covered the indicated pH values as determined by measurement with a glass electrode.[7]

Polarographic measurements on the polyene aldehydes were made in 50% aqueous dioxane solutions prepared by dilution of the stock buffer solutions with dioxane purified as previously described.[1] The pH values mentioned

(1) Blout and Fields, THIS JOURNAL, **70**, 189 (1948).

(2) Blout, Fields and Karplus, *ibid.*, **70**, 194 (1948).

(3) Adkins and Cox, *ibid.*, **60**, 1151 (1938), report the polarographic reduction of crotonaldehyde, benzalacetone, cinnamalacetophenone, dibenzalacetone and several other unsaturated carbonyl compounds in tetramethylammonium hydroxide solution and in ammonium chloride solution.

(4) Semerano and Chisini, *Gazz. chim. ital.*, **66**, 510 (1936).

(5) Schwaer, *Collection Czechoslov. Chem. Commun.*, **7**, 326 (1935), found that α,β unsaturated acids of the maleic acid type were reducible in 1 N hydrochloric acid solution. Whereas sorbic acid was reducible in alkaline solution at a highly negative potential, crotonic and itaconic acids could not be reduced before the decomposition of the supporting electrolyte occurred.

(6) Lingane and Kolthoff, THIS JOURNAL, **61**, 825 (1939).

(7) Coleman Electric Company, Model 3A Electrometer.

Stock buffer	Components	pH Range of buffer dil. with H_2O	pH Range of buffer dil. with $C_4H_8O_2$
A	0.2 M NaOAc–HCl	1.2–3.2	1.1–4.4
B	0.2 M NaOAc–HOAc	3.9–5.8	5.3–7.2
C	0.2 M NaOH–NH$_4$Cl	8.6–10.5	8.4–10.4

throughout the rest of this discussion refer to the solutions 50% in dioxane and are uncorrected for the non-aqueous solution error of the glass electrode.[8] For that reason they are nominal values only.

For comparison of the polarographic behavior of members of this series it was desirable to use solutions of approximately the same concentration of supporting electrolyte throughout. The solubility characteristics of this series of aldehydes led to the choice of the particular solvent and buffer solutions used. Since the higher members of the series, particularly 2,4,6,8,10-dodecapentaenal, are only slightly soluble even in 50% aqueous dioxane solution, it was necessary in some cases to employ a solution whose buffer capacity is less than that desirable for polarographic work. The complications which this factor introduces in the interpretation of some of our data will be discussed in the sequel.

Procedure.—Because the aliphatic polyene aldehydes are relatively unstable the stock solutions of the compounds in dioxane were not allowed to stand more than three hours before measurement. The solutions of the aldehydes in the appropriate buffers were deaerated in the usual manner for twenty to thirty minutes with nitrogen purified by passage through a tube filled with freshly-reduced copper filings maintained at 450–500°. All potentials were measured against a saturated calomel electrode (S. C. E.) and the values recorded in this paper have been corrected for the iR drops of the solutions. Diffusion currents were corrected for the residual current of the supporting electrolyte. Measurements were made at 25 ± 0.5°.

Results and Discussion

The characteristics of the polarographic curves of the unsaturated aldehydes in acid, essentially neutral, and basic solutions may be seen in Figs. 1 to 5. Each of the compounds studied shows at least one well-defined wave in the pH range of 1 to 11. In addition a second polarographic wave of approximately the same height as the first is observed for each compound over a more limited pH range. The initial appearance of the second wave occurs at progressively lower pH values as the number of double bonds is increased. Although the first wave of each substance is well defined over the pH range investigated, the second tends to become less distinct in the most alkaline solutions.

As can be seen from Table I the values of the ratio $i_d/Cm^{2/3}t^{1/6}$ of the first wave are essentially independent of pH for all the unsaturated aldehydes. Moreover, the average value of this ratio is, to a first approximation, unaffected by the number of carbon–carbon double bonds conjugated with the carbonyl group; the slight de-

(8) Dole, "The Glass Electrode," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 139.
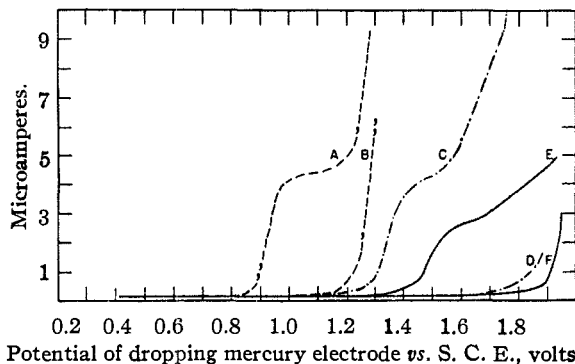
Potential of dropping mercury electrode vs. S. C. E., volts.

Fig. 1.—Polarograms of crotonaldehyde in buffered 50% aqueous dioxane solutions: A, pH 1.3, concentration 1.38 × 10⁻³ M; B, pH 1.3, solvent blank; C, pH 8.3, concentration 1.44 × 10⁻³ M; D, pH 8.3, solvent blank; E, pH 10.4, concentration 0.84 × 10⁻³ M; F, pH 10.4, solvent blank.

Potential of dropping mercury electrode vs. S. C. E., volts.
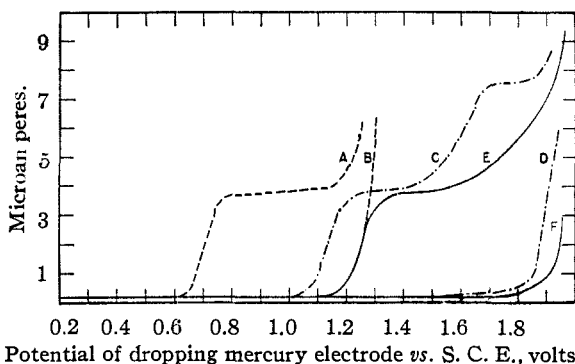
Fig. 2.—Polarograms of 2,4-hexadienal in buffered 50% aqueous dioxane solutions: A, pH 1.3, concentration 1.32 × 10⁻³ M; B, pH 1.3, solvent blank; C, pH 8.3, concentration 1.29 × 10⁻³ M; D, pH 8.3, solvent blank; E, pH 10.4, concentration 1.43 × 10⁻³ M; F, pH 10.4, solvent blank.
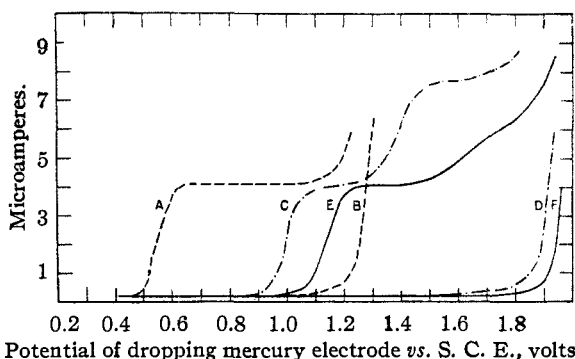

Potential of dropping mercury electrode vs. S. C. E., volts.

Fig. 3.—Polarograms of 2,4,6-octatrienal in buffered 50% aqueous dioxane solutions: A, pH 1.3, concentration 1.42 × 10⁻³ M; B, pH 1.3, solvent blank; C, pH 8.3, concentration 1.44 × 10⁻³ M; D, pH 8.3, solvent blank; E, pH 10.4, concentration 1.44 × 10⁻³ M; F, pH 10.4, solvent blank.

crease in these ratios with increasing molecular weight probably arises from diminished diffusion
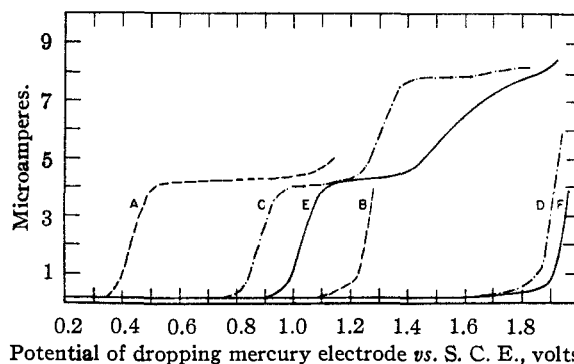

Potential of dropping mercury electrode vs. S. C. E., volts.

Fig. 4.—Polarograms of 2,4,6,8-decatetraenal in buffered 50% aqueous dioxane solutions: A, pH 1.3, concentration 1.70 × 10⁻³ M; B, pH 1.3, solvent blank; C, pH 8.4, concentration 1.62 × 10⁻³ M; D, pH 8.4, solvent blank; E, pH 10.4, concentration 1.68 × 10⁻³ M; F. pH 10.4, solvent blank.

Potential of dropping mercury electrode vs. S. C. E., volts.
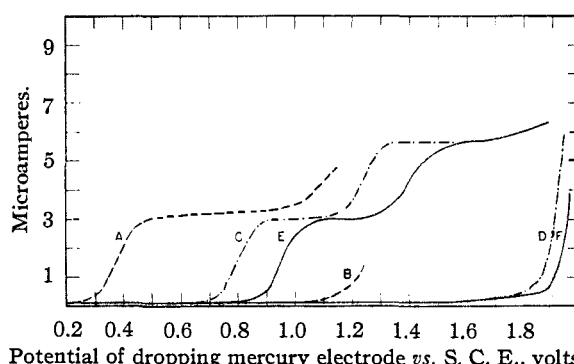
Fig. 5.—Polarograms of 2,4,6,8,10-dodecapentaenal in buffered 50% aqueous dioxane solutions: A, pH 1.3, concentration 1.28 × 10⁻³ M; B, pH 1.3, solvent blank; C, pH 8.4, concentration 1.08 × 10⁻³ M; D, pH 8.4, solvent blank; E, pH 10.3, concentration 1.19 × 10⁻³ M; F, pH 10.3, solvent blank.

coefficients rather than a change in the electron requirements of the waves. Furthermore, the near equivalence of the $i_d/Cm^{2/3}t^{1/6}$ ratios for the first and second waves of each compound except crotonaldehyde makes it probable that the n-values of the two waves are identical. The variations in the diffusion current for the first wave of crotonaldehyde are probably to be attributed to losses of varying quantities of this volatile compound during deaeration with nitrogen. Since the second wave of crotonaldehyde does not attain its limiting value before decomposition of the supporting electrolyte occurs, accurate measurement of its diffusion current and half-wave potential is difficult. The $i_d/Cm^{2/3}t^{1/6}$ ratios for 2,4-hexadienal are somewhat lower than might be expected from the values of the ratios for the higher members of the series; this may arise from the greater instability of this compound as compared with the more highly conjugated aldehydes.

In Fig. 6 we have plotted for the polyene alde-

TABLE I

Crotonaldehyde

pH	1.3	2.3	3.1	4.2	5.2	6.3	7.2	8.3	9.2	10.4	11.1
$i_d/Cm^{2/3}t^{1/6}$	1.58	1.51	1.52	1.29	1.16	1.61	1.61	1.63	1.48	1.61	1.45

2,4-Hexadienal

pH	1.3	2.1	3.1	4.3	5.2	6.3	7.2	8.3	9.1	10.4	11.3
$i_d/Cm^{2/3}t^{1/6}$	1.43	1.46	1.35	1.35	1.35	1.38	1.34	1.48 (1.52)[a]	1.43 (1.57)	1.35	1.37 (0.21)

2,4,6-Octatrienal

pH	1.3	2.4	3.3	4.1	5.2	6.3	7.2	8.3	9.2	10.4	11.0
$i_d/Cm^{2/3}t^{1/6}$	1.45	1.40	1.42	1.38	1.39	1.40 (1.09)	1.46 (1.12)	1.42 (1.33)	1.42 (1.25)	1.45	1.48

2,4,6,8-Decatetraenal

pH	1.3	2.3	3.4	4.2	5.2	6.3	7.0	8.4	9.3	10.4	11.0
$i_d/Cm^{2/3}t^{1/6}$	1.29	1.33	1.34	1.28	1.30	1.29 (1.20)	1.30 (1.09)	1.28 (1.20)	1.29 (1.24)	1.33 (1.09)	1.30 (1.07)

2,4,6,8,10-Dodecapentaenal

pH	1.3	2.3	3.1	4.1	5.1	6.0	7.0	8.4	9.3	10.3
$i_d/Cm^{2/3}t^{1/6}$	1.25	1.22	1.22	1.30 (0.94)	1.20 (1.08)	1.26 (1.14)	1.31 (1.14)	1.34 (1.38)	1.33 (1.36)	1.29 (1.25)

[a] The values in parentheses refer to the second wave.

hydes the half-wave potentials of the first wave $(E_{\frac{1}{2}})_1$ and of the second wave $(E_{\frac{1}{2}})_2$ for several pH values as a function of the number of carbon–carbon double bonds. The addition of another C=C to an aliphatic polyene aldehyde with x double bonds causes a shift in $(E_{\frac{1}{2}})_1$ toward less negative potentials; that is, the ease of reduction increases with the number of double bonds conjugated with the carbonyl group. It is noted, however, that the increment per double bond decreases as the chain is lengthened.[9] Thus, while the $(E_{\frac{1}{2}})_1$ values for 2,4-hexadienal are on the average 0.23 volt more positive than those for crotonaldehyde, the $(E_{\frac{1}{2}})_1$ values for 2,4,6,8,10-dodecapentaenal are on the average only 0.07 volt more positive than those for 2,4,6,8-decatetraenal.
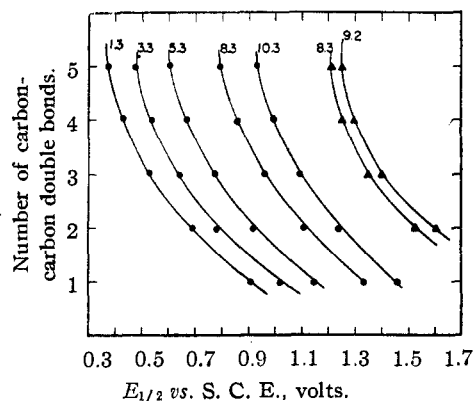

Fig. 6.—Half-wave potentials vs. number of carbon–carbon double bonds: —●—●—, first wave —▲—▲—, second wave. The number beside each curve refers to the pH at which measurements were made.

A plausible explanation for the direction of the shift of $(E_{\frac{1}{2}})_1$ with x can be given if we assume that in the reaction which produces the first polarographic wave the electrode-active species are the aldehyde (I) and the conjugate acid (II) of the

(9) This effect is similar to that observed in the ultraviolet and infra-red spectra of these compounds where the shift in the position of at least one of the absorption maxima seems to become smaller as the length of the conjugated system is increased.[1,2]

radical-ion formed by a one-electron reduction of the parent substance.[10] The formation of the radical II may be followed by its dimerization to produce, perhaps, the unsaturated glycol III. Although dimerization of the initially-formed radicals makes the over-all electrode reaction an irreversible process, the step involving electron transfer may very well be a reversible one. The significance of the half-wave potentials for systems of this type is the same as for reversible ones.

$$CH_3(CH=CH)_x—CHO + H^+ + e \rightleftharpoons$$
$$CH_3(CH=CH)_x—\dot{C}HOH \longrightarrow$$
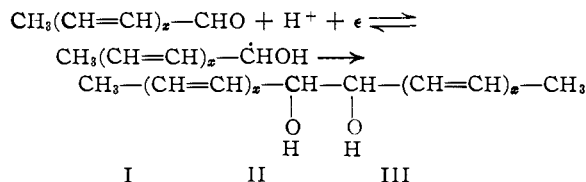
Since the nature of the electrode and other experimental conditions remained constant throughout, on the basis of the foregoing assumptions the change in the $(E_{\frac{1}{2}})_1$ values at constant pH affords a measure of the change in the relative stabilities
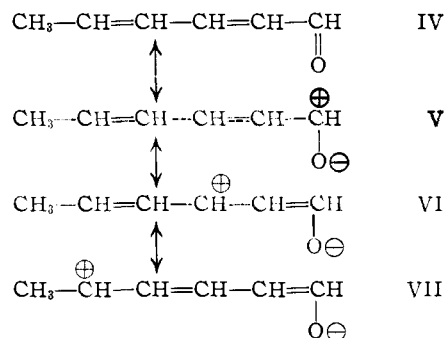
(10) The bimolecular reductions of carbonyl compounds are well known. Familiar examples which may be mentioned are the electrolytic reduction of anisaldehyde to a mixture of the pinacols, hydroanisoin and iso-hydroanisoin,[a] the reduction of crotonaldehyde and cinnamaldehyde with zinc-copper couple to dipropenyl glycol[b] and hydrocinnamoin,[c] respectively, and the reduction of aromatic and unsaturated aldehydes with vanadous salts to the corresponding pinacols.[d] (a) Law, J. Chem. Soc., 89, 1512 (1906). (b) Young, Levanas and Jasaitis, THIS JOURNAL, 58, 2274 (1936). (c) Kuhn and Winterstein, Ber., 60, 432 (1927). (d) Conant and Cutter, THIS JOURNAL, 48, 1016 (1926).
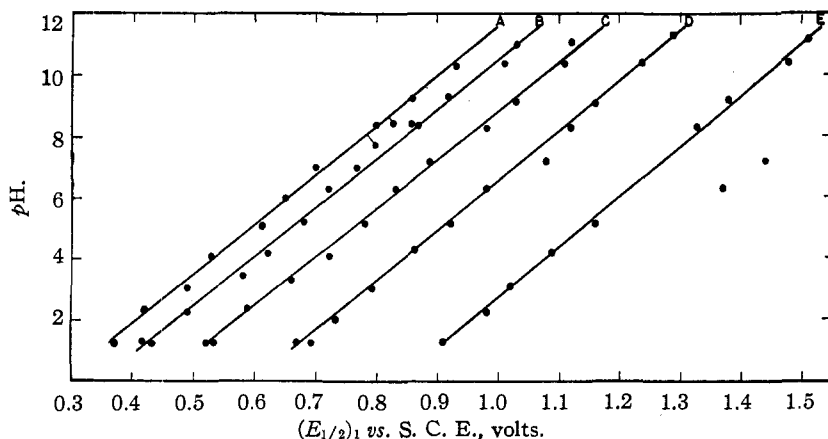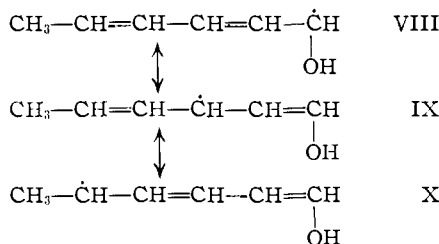
Fig. 7.—Half-wave potential of first wave vs. pH for: A, 2,4,6,8,10-dodecapentaenal; B, 2,4,6,8-decatetraenal; C, 2,4,6-octatrienal; D, 2,4-hexadienal; E, crotonaldehyde.

of the aldehyde and its related free radical on going from one member of the series to the next.

An aliphatic polyene aldehyde such as 2,4-hexadienal may be represented as a hybrid of the classical form, IV, and ionic forms such as V through VII.

On the other hand, the major contributing forms of the corresponding free radical, structures VIII-X, all contain the same number of the same kinds of bonds, do not involve charge separation and are probably of approximately equal energy. The resonance energy of the radical, therefore, is probably greater than that of its related aldehyde.

$$CH_3—CH=CH—CH=CH—\dot{C}H \quad VIII$$
$$\updownarrow$$
$$\overset{|}{OH}$$

$$CH_3—CH=CH—\dot{C}H—CH=CH \quad IX$$
$$\updownarrow$$
$$\overset{|}{OH}$$

$$CH_3—\dot{C}H—CH=CH—CH=CH \quad X$$
$$\overset{|}{OH}$$

While the resonance energy of a polyene aldehyde as well as that of the corresponding radical would be expected to increase with the length of the conjugated system, each additional double bond should lead to a relatively greater stabilizaton of the radical than of the aldehyde. This factor would account for the direction of the shift. The decrease in the magnitude of the change in $(E_\frac{1}{2})_1$ per double bond noted for the higher members of the series can be correlated with the fact that as x is increased each additional double bond produces a proportionately smaller increase in the number of equivalent forms contributing to the structure of the aldehyde and the free radical and, thus, probably also a smaller change in the relative stabilities of the aldehyde and its reduction product.

For the five polyene aldehydes studied $(E_\frac{1}{2})_1$ is an approximately linear function of pH (Fig. 7); in each case a unit increase in pH shifts the half-

wave potential to more negative values by 0.06 volt. In the measured pH range 6–8 two points on the crotonaldehyde curve and one on the hexadienal curve deviate markedly from the straight lines which fit all the remaining data. Although the buffer capacity of the pH 6 and especially the pH 7 supporting electrolytes are quite low, it appears unlikely that the deviations of the half-wave potentials of crotonaldehyde and hexadienal arise from this cause. No such pronounced deviations in this pH region are observed for the other (more stable) compounds which were studied at approximately the same concentrations and in solutions of the same compositions. For a thermodynamically reversible reaction such a dependence of $E_\frac{1}{2}$ would indicate that the reduction product differed from its oxidized form by one hydrogen atom. It is interesting to note that in the electrode reactions under consideration the variation of $(E_\frac{1}{2})_1$ with pH conforms closely to that anticipated for the reversible case.

The second half-wave potential, like the first, shifts toward less negative values as the number of double bonds is increased (Fig. 8). The increment of $(E_\frac{1}{2})_2$ for those members of the series which show a well-defined second wave decreases with increasing chain length in much the same manner as observed with $(E_\frac{1}{2})_1$.
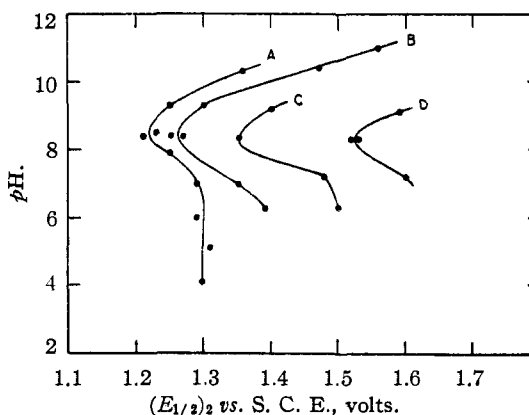
Fig. 8.—Half-wave potential of second wave vs. pH for: A, 2,4,6,8,10-dodecapentaenal; B, 2,4,6,8,-decatetraenal; C, 2,4,6-octatrienal; D, 2,4-hexadienal.

The second wave is well defined in most cases only in solutions more alkaline than pH 6; generally, in acid solutions this wave merges with or is obscured by that due to decomposition of the supporting electrolyte. For 2,4,6,8,10-dodecapentaenal a distinct second wave is obtained over

the pH range of 4 to 10 and in acid solutions $(E_{\frac{1}{2}})_2$ seems to be independent of pH. In all the compounds studied the plot of $(E_{\frac{1}{2}})_2$ vs. pH shows a minimum in the region of pH 8. A possible explanation for this unusual behavior may be the low buffer capacity of some of the supporting electrolytes used. Further work on this point is now in progress.

Calculation of Diffusion Coefficients.—The diffusion coefficient, D, of a substance which undergoes oxidation or reduction at the dropping mercury electrode can be calculated from the Ilkovic equation[11] $i_d = 605nD^{1/2}Cm^{2/3}t^{1/6}$. We
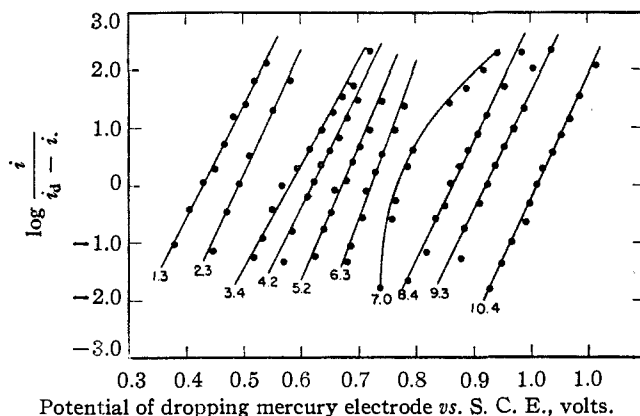

Fig. 9.—Plots of log $i/(i_d - i)$ vs. potential of the dropping mercury electrode for 2,4,6,8-decatetraenal. The number beside each curve refers to the pH at which measurements were made.

have calculated the diffusion coefficients of each of the five unsaturated aldehydes investigated using the average values of the diffusion currents for the first and second waves and assuming that each wave corresponds to a one-electron reduction. The values found are listed in Table II.

TABLE II

Compound	D (cm.^{2} sec.$^{-1}$)
Crotonaldehyde	6.1×10^{-6}
2,4-Hexadienal	5.3×10^{-6}
2,4,6-Octatrienal	5.1×10^{-6}
2,4,6,8-Decatetraenal	4.3×10^{-6}
2,4,6,8,10-Dodecapentaenal	4.2×10^{-6}

In all cases the drop time used in these calculations was measured at the same potential as the diffusion current. The diffusion coefficient recorded above for crotonaldehyde is probably somewhat below the actual value because the loss of this rather volatile aldehyde during deaeration results in a decrease in the actual concentration of the material below the original value. This loss of aldehyde results in a lower diffusion current and hence a lower diffusion coefficient. All the higher aldehydes have sufficiently low vapor pressures so that the error from this source is probably negligible. The value of the diffusion coefficient of 2,4-

(11) Kolthoff and Lingane, "Polarography," Interscience Publishers. New York, N. Y., 1941, p. 30.

hexadienal is probably low, possibly as a result of some decomposition of this relatively unstable compound during deaeration and measurement.

Reversibility of Electrode Reactions.—For a reversible reaction at a constant pH at 25° the potential of the dropping mercury electrode is related to the current at any point on the polarographic wave by the equation

$$E_{d.e.} = E_{\frac{1}{2}} - \frac{0.059}{n} \log \frac{i}{i_d - i}$$

If log $i/(i_d - i)$ is plotted as a function of $E_{d.e.}$, a straight line is obtained from the slope of which the number of electrons involved in the electrode reaction can be calculated. It is observed experimentally that many irreversible reactions obey the related equation

$$E_{d.e.} = E_{\frac{1}{2}} - \frac{0.059}{\alpha} \log \frac{i}{i_d - i}$$

and also yield linear plots of log $i/i_d - i)$ vs. $E_{d.e.}$. In these cases, α is not necessarily an integer and may even be less than 1. An exact interpretation of the polarographic waves obtained in such cases has not yet been presented.

We have plotted for the first polarographic wave of each of the five unsaturated aldehydes log $i/(i_d - i)$ as a function of $E_{d.e.}$ and have found approximately linear relationships at many of the pH values examined. The curves shown in Fig. 9 for 2,4,6,8-decatetraenal are typical of those obtained for the other members of the series. Table III lists the values calculated from the slopes of the straight lines mentioned above or from the slopes of the tangents to the curves at the half-wave potentials.

TABLE III

Crotonaldehyde

pH	1.3	2.3	3.1	4.2	5.2					
α	1.7	1.8	1.3	1.2	1.1					

2,4-Hexadienal

pH	1.3	2.1	3.1	4.3	5.2	8.3	9.1	10.4		
α	1.4	1.8	1.4	1.5	1.2	1.2	1.3	1.0		

2,4,6-Octatrienal

pH	1.3	2.4	3.3	4.1	5.2	6.3	8.3	9.2	10.4	
α	2.0	1.7	1.3	1.4	1.6	1.7	1.1	1.6	1.1	

2,4,6,8-Decatetraenal

pH	1.3	2.3	3.4	4.2	5.2	6.3	7.0	8.4	9.3	10.4
α	1.2	1.3	1.0	1.1	1.3	1.6	1.6	1.2	1.2	1.2

2,4,6,8,10-Dodecapentaenal

pH	1.3	2.3	3.1	4.1	5.1	6.0	7.0	8.4	9.3	10.3
α	1.4	0.9	0.9	0.8	1.1	1.1	1.2	1.2	1.2	1.0

The deviation from linearity of the curve for 2,4,6,8-decatetraenal at pH 7 quite probably arises from the low buffer capacity of this supporting electrolyte. Some of the high α-values may also be due to this cause or to a degree of irreversibility in the electrode reaction.

Although the relationship between $E_{d.e.}$ and

$\log i/(i_d - i)$ affords a convenient and reliable means of determining the n-values of reversible electrode reactions, other methods are generally used when dealing with irreversible reactions. The Ilkovic equation can be used to calculate the n-values of irreversible as well as reversible electrode reactions, but the paucity of diffusion coefficient data severely limits the usefulness of this procedure. Coulometric measurements afford the most reliable means of determining n- values in irreversible reactions.[12] Such measurements for the aliphatic polyene aldehydes will be reported in a later paper.

(12) Lingane, THIS JOURNAL, **67**, 1916 (1945).

Acknowledgment.—We wish to express our appreciation to Mr. Marshall Kane, who assisted in the preparation and measurement of many of these compounds.

Summary

The polarographic behavior of aliphatic polyene aldehydes has been examined in buffered 50% dioxane solution over the pH range 1 to 11. The variations in half-wave potentials and the $i_d/Cm^{2/3}t^{1/6}$ ratios have been examined as functions of pH and the number of double bonds in the molecule.

CAMBRIDGE 39, MASSACHUSETTS

[CONTRIBUTION FROM THE ATLANTIC REFINING CO.]

The Isolation and Physical Properties of the Diisopropylbenzenes

BY F. W. MELPOLDER, J. E. WOODBRIDGE AND C. E. HEADINGTON

Introduction

The physical properties of the isomeric diisopropylbenzenes reported in the literature are fragmentary and the wide variations in these values indicate that only incomplete separations of the isomers have previously been accomplished.[1-7] Newton,[8] however, isolated meta and para diiso-

TABLE I

PHYSICAL PROPERTIES OF THE ISOMERIC DIISOPROPYL-BENZENES

Property	Found by this study Ortho	Meta	Para	Found by Newton[8] Meta	Para
Purity, mole %	99.6	99.6	99.8		
Melting point, °C.	−56.68	−63.13	−17.07		
Cryoscopic constant, mole frac./°C.	0.0221	0.0285	0.0292		
Boiling point, °C. { 760 mm.	203.75	203.18	210.37	203.0	210.3
300 mm.	168.33	167.83	174.4	168.9[b]	174.4[b]
100 mm.	133.9	133.4	139.3		
50 mm.	115.4	114.9	120 2		
Antoine constants[a] { A	6.9800	6.9805	7.0667	7.1710[b]	7.0726[b]
B	1619.5	1616.6	1711.9	1766.4[b]	1709.2[b]
C	191.33	191.15	198.59	207.40[b]	197.51[b]
Refractive index { 20°	1.49603	1.48883	1.48983	1.4884	1.4895
25°	1.49373	1.48748	1.48758		
Specific dispersion 25°	157	155	157		
Density, g./ml. 20°	0.87007	0.85593	0.85676	0.8566	0.8571
Molecular weight	161.93	161.38	162.67		
Carbon-hydrogen ratio	7.96	7.92	7.91		

[a] Antoine equation, $\log_{10} P = A - B/(C + t)$, P = pressure, mm. t = boiling point, °C. [b] Calculated from data of Newton.

(1) V. N. Ipatieff, B. B. Corson and H. Pines, THIS JOURNAL, **58**, 919 (1936).

(2) V. N. Ipatieff and H. Pines, ibid., **59**, 56 (1937).

(3) T. U. Ju, C. E. Wood and F. H. Gorner, J. Inst. Petr., **28**, 159 (1942).

(4) J. F. McKenna and F. J. Sowa, THIS JOURNAL, **59**, 470 (1937).

(5) S. J. Slanina, F. J. Sowa and J. A. Nieuwland, ibid., **57**, 1547 (1935).

(6) D. R. Stull, Ind. Eng. Chem., **39**, 517 (1947).

(7) Uhlhorn, Ber., **23**, 3142 (1890).

(8) A. Newton, THIS JOURNAL, **65**, 320 (1943).

propylbenzene by distillation from a propylated benzene which apparently contained none of the ortho isomer. The physical properties reported by him for the two isomers are in substantial agreement with those found by the authors in the work to be described (Table I).

In this work the isolation of substantially pure ortho, meta, and para diisopropylbenzenes from benzene–propylene alkylate was accomplished by a combination of distillation, fractional crystallization, adsorption, sulfonation, and hydrolysis. Precise physical properties as well as ultraviolet, infrared and mass spectra are reported on each of the isomers.

Initial Separation.—The source of these compounds was a high boiling by-product fraction, b. p. 200–215°, produced by a commercial process for making cumene wherein benzene is alkylated with propylene over U. O. P. phosphoric acid catalyst. To roughly determine the distribution of the isomeric diisopropylbenzenes in the mixture a 700-cc. volume was fractionally distilled through a 100-plate Heligrid column into 5% cuts. Although the distillation curve (Fig. 1) exhibits only two boiling point flats, the refractive index curve indicates that at least two distinct compounds are present in fraction I, b. p. 203–204°, and one in fraction II, b. p. 210–211°. Inspection of the refractive indices and ultraviolet spectra indicated that the material present in fraction I contained a major amount of meta diisopropylbenzene and a minor concentration of the ortho isomer, while fraction II, comprising nearly half of the crude mixture, was largely para isomer. The next step was therefore to distil 15 liters of the charge stock into two fractions, one boiling at 203–204° and the other at 210–211°.

Separation of o- from m-Diisopropylbenzene.—It was found that repeated high efficiency distillations of the 203–204°, material resulted in only a partial separation of ortho and meta isomers. The best distillate fraction of ortho isomer froze to a viscous partially crystalline mass at −80° whereas the meta isomer fraction crystallized with some difficulty at −72°.

Since m-xylene was successfully purified by Mair, Termini, Willingham and Rossini[9] by the selective sul-

(9) B. J. Mair, D. J. Termini, C. B. Willingham and F. D. Rossini, J. Res. Nat. Bur. Stds., **37**, 229 (1946).