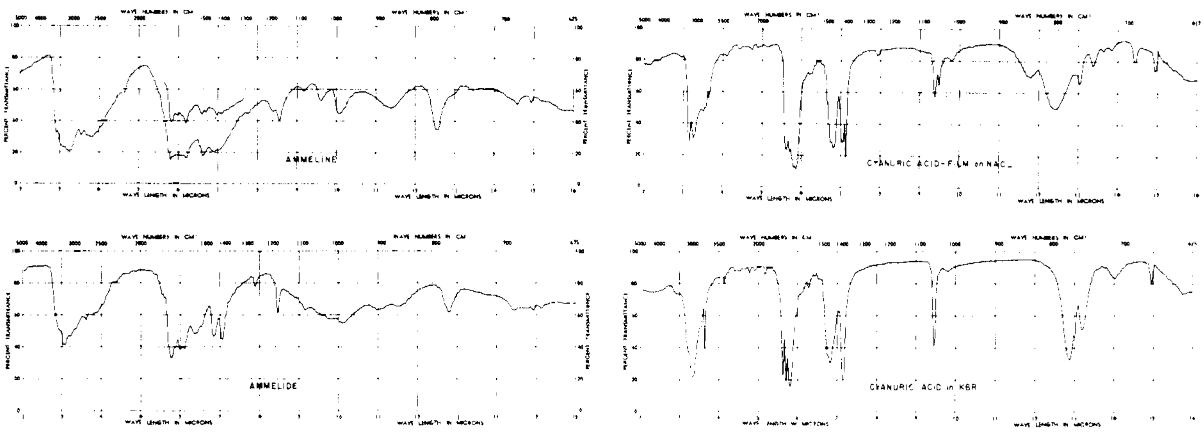

Fig. 6.—Spectra of ammeline, ammelide and cyanuric acid.

means the triazine ring conjugation would be conserved. With cyanuric acid the situation is much more certain, since the spectrum clearly supports other investigations[10,11] in showing cyanuric acid to favor the "iso" or amido form. In brief, although the spectra portray quite clearly the progression from the conjugated ring structure of melamine to the completely "iso" structure of cyanuric acid, it is difficult to say at what position the equilibrium lies in solid ammeline and ammelide. The spectrum of ammeline does, however, provide some evidence for conservation of the conjugated-ring form.

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TEXAS CITY, TEXAS

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[10] E. H. Wiebenga, THIS JOURNAL, **74**, 6156 (1952).

[11] R. Newman and R. M. Badger, *ibid.*, **74**, 3545 (1952).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF EMORY UNIVERSITY]

Polarographic Reduction of Some Aromatic Aldehydes

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The polarographic reduction of benzaldehyde and ten other aromatic aldehydes has been studied in buffered solutions in the *p*H range 1 to 13. A number of macroelectrolyses have been run at controlled potentials under varying experimental conditions. Products were isolated and the number of electrons consumed in the reduction process measured. The effect of substituents in the benzene nucleus on the second wave found in certain solutions of high *p*H is discussed. Further evidence is reported for the correlation between the separation of the two waves in basic media and the tendency of groups in the molecule to stabilize a free radical intermediate.

The polarographic reduction of benzaldehyde and many other aromatic aldehydes has been studied by numerous investigators,[1-7] and much of this work is summarized in two treatises on polarography.[8,9] The behavior of most of the simpler aromatic aldehydes as well as ketones is consistent with the mechanism summarizd by Ashworth[3] and Milner.[9] The influence of substituents in the benzene nucleus of benzaldehyde, however, often leads to variations in the normal pattern of behavior,[4] and other factors, such as type and concentration of buffer as well as the presence of certain electrolytes, may produce anomalous waves. Differences in behavior are most pronounced in strongly alkaline media where one, two and even three waves are sometimes observed with certain carbonyl compounds.[10]

The present work was undertaken to study the influence of certain nuclear substituents on the behavior of aromatic aldehydes. We were particularly interested in determining whether or not variations in behavior were consistent with the effects which one would predict from the structure of the aromatic molecule in terms of the mecha-

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[1] M. Tokuoka, *Collection Czechoslov. Chem. Communs.*, **7**, 392 (1935).

[2] R. Pasternak, *Helv. Chim. Acta*, **31**, 753 (1948).

[3] M. Ashworth, *Collection Czechoslov. Chem. Communs.*, **13**, 229 (1948).

[4] I. A. Korshunov and L. N. Sazanova, *Zhur. Fiz. Khim.*, **23**, 202 (1949).

[5] H. J. Gardner, *Chemistry & Industry*, **29**, 819 (1951).

[6] R. N. Schmid and E. Heilbronner, *Helv. Chim. Acta*, **37**, 1453 (1954).

[7] L. Holleck and H. Marsen, *Z. Elektrochem.*, **57**, 301, 944 (1953).

[8] I. M. Kolthoff and J. J. Lingane, "Polarography," Second Ed., Vol. II, Interscience Publishers, Inc., New York, N. Y., 1952, p. 678.

[9] G. W. C. Milner, "The Principles and Applications of Polarography," Longmans, Green and Co., New York, N. Y., 1956, p. 501.

[10] R. A. Day, Jr., S. R. Milliken and W. D. Shults, THIS JOURNAL, **74**, 2741 (1952).

nism referred to above.[3,9] To this end we have studied the polarographic reduction of benzaldehyde and ten other aromatic aldehydes in the pH range 1 to 13. We also have studied the electrolysis at controlled potential of some of these compounds, measuring the number of electrons consumed in the reduction as well as isolating products under various experimental conditions.

Experimental

The polarographic data were obtained with a Leeds and Northrup Electrochemograph Type E. Half-wave potentials were corrected for IR drop and for lag caused by galvanometer damping. The electrolysis cell, experimental procedure and buffer solutions were the same as previously described[10] except that veronal buffers were used in the pH range 8 to 9.5 and phosphate buffers in the range 11 to 12. All cell solutions were 25% by volume of 95% ethanol and the aldehyde concentration was normally 0.00025 to 0.0010 M. A single capillary of Corning marine barometer tubing was used. Its characteristics were: droptime 6.0 sec., m = 1.291 mg./sec. determined in 25% ethanol, citrate–phosphate buffer of pH 5.5 with an open circuit.

The macroelectrolyses were carried out using a potentiostat of the Lingane–Jones type.[11] For coulometric measurements a hydrogen–oxygen coulometer was employed. The cell, electrodes and experimental procedures were essentially those recommended by Lingane.[12] Typical results obtained with 2-naphthaldehyde are as follows: pH 2.2, −1.15 v., n = 0.8, product 1,2-di-β-naphthyl-1,2-ethanediol, m.p. 251° (cor.); pH 7.3, −1.65 v., n = 1.8, product β-naphthylcarbinol, m.p. 77–79° (uncor.); 0.10 M NaOH, −1.75 v., n = 1.0, product 1,2-di-β-naphthyl-1,2-ethanediol, m.p. 251° (cor.); calcium hydroxide–calcium chloride buffer,[13] pH 12.0, −2.0 v., n = 1.8, product β-naphthylcarbinol, m.p. 76–78° (uncor.). Some additional results obtained with piperonal were: 0.01 M NaOH, −1.85 v., n = 1.1, product 3,4,3′,4′-bis-methylenedioxyhydrobenzoin, m.p. 197–199° (uncor.); pH 6.0, −1.65 v., product piperonyl alcohol, m.p. 50–53° (uncorr.).

Results and Discussion

The results of the polarographic studies are summarized in Table I. The half-wave potentials designated $E_{1/2}{}^1$ and $E_{1/2}{}^2$ refer to the two single-electron waves normally observed with aromatic carbonyl compounds in acid media. These waves usually merge about pH 5 to 6 to give a single two-electron wave, here designated $E_{1/2}$.[12] At higher pH values the latter wave often decreases in height and another wave, here designated $E_{1/2}{}^3$, appears at more negative potentials. The normal pattern for the variation with pH of the half-wave potentials of these waves is shown in Fig. 1. In solutions of low pH, wave 2 often is masked by hydrogen discharge, and a single one-electron wave only is observed. We have listed in Table I a pH value at which such behavior is observed for each aldehyde. We have also listed a higher pH at which both acid waves are observed, as well as a pH value at which these two waves are merged into a single wave of full current (two electrons).

In solutions of high pH, for example 0.010 to 0.10 M NaOH, the height of the single wave shown by aromatic aldehydes drops to about half the value shown in more acid media.[3,6,7,14] We have also listed in Table I a pH value at which such behavior was found for each aldehyde. Finally we have included data for conditions under which wave 3 can be observed separated from wave 1–2 in solutions of high pH. Wave 3 frequently is masked by reduction of the cation of the supporting electrolyte, but it often can be observed in solutions containing calcium or tetraalkylammonium ions.[3]

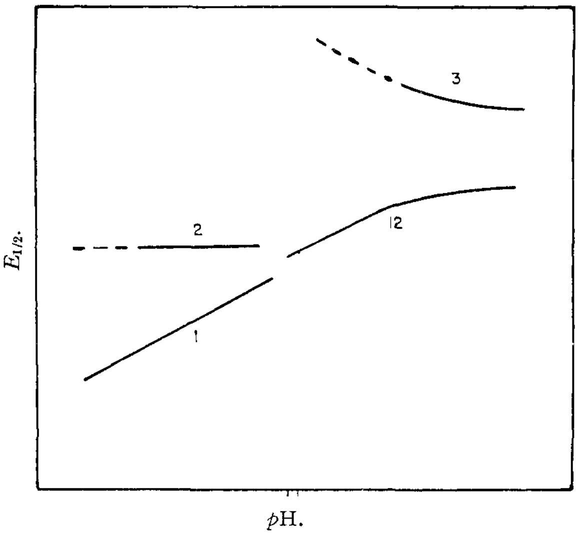

Fig. 1.—Variation with pH of half-wave potentials of polarographic waves of carbonyl compounds.

It is readily apparent from the table that the behavior of all of these aldehydes is qualitatively the same.[15] Most of these compounds have been reported to reduce in a single one-electron step in strongly alkaline media, such results having been obtained under conditions such that wave 3 was masked by reduction of the supporting electrolyte. One of the compounds, p-dimethylaminobenzaldehyde, has been reported to behave differently from benzaldehyde, reducing in two steps only between pH 5 and 6.7.[4] The potential of the first acid wave was reported to be constant from pH 5 to 7 and this wave was not found in solutions of higher pH.[4,8] Actually the second acid wave (wave 2) occurs at such negative potentials that it is masked by hydrogen discharge over the entire pH range of about 1 to 7. Under our experimental conditions we were able to observe wave 2 only over a short pH range of about 7.5 to 8.5, and then it was necessary to work at fairly low concentrations of aldehyde to avoid a strong maximum. At higher pH values waves 1 and 2 are merged in the usual fashion, but this merger occurs at a somewhat higher pH than normal.

The reason for the decrease in height of the single wave in basic media and the appearance of wave 3 has been the subject of much speculation. Ashworth[3] assumed that a metal ketyl was formed as the intermediate in basic media and was in reversible equilibrium with the dimeric form[16]

$$2R_2\dot{C}\text{–}O^-M^+ \rightleftharpoons R_2C(O^-M^+)C(O^-M^+)R_2$$

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[11] J. J. Lingane and S. L. Jones, *Anal. Chem.*, **22**, 1169 (1950).

[12] J. J. Lingane, "Electroanalytical Chemistry," Interscience Publishers, Inc., New York, N. Y., 1953, p. 251.

[13] W. M. Tuddenham and D. H. Anderson, *Anal. Chem.*, **22**, 1146 (1950).

[14] R. A. Day, Jr., THIS JOURNAL, **76**, 280 (1954).

[15] The effect of substituents on the value of the half-wave potential of the first acid wave of carbonyl compounds has been reported in many investigations. We will not discuss this relationship here.

[16] Metal ketyls are ionic and show reactions which depend upon the solvent. The extent of dissociation of the ion pair is influenced by the metal involved.

Wave 3 was attributed to the reduction of the metal ketyl to the carbinol. The reason for the separation of wave 1–2 and wave 3 under certain conditions was explained in terms of the extent to which the equilibrium favored formation of the dimer. In cases where the concentration of metal ketyl is greatly decreased by dimerization, the intermediate is not reduced at its formation potential, but a more negative potential is required. Hence the two waves are more likely to be separate. Elving[17] has questioned the validity of postulating a metal ketyl in aqueous media and has obtained evidence that the intermediate (in the case of aliphatic–aromatic ketones) is the carbinolate free radical ion. He attributes wave 3 to the reduction of the latter ion

$$R_2\dot{C}\text{–}O^- + e^- + 2H^+ = R_2CHOH$$

This ion is not reduced at its formation potential because the ion is repelled by the electrode and the electron effecting the reduction must enter an area of increased electron density. Holleck and Marsen,[7] in the case of benzaldehyde, also assume that a carbinolate free radical ion is the intermediate in basic solution and write its irreversible dimerization to hydrobenzoin.[18] They did not work, however, under conditions such that wave 3 was observed.

TABLE I

$E_{1/2}{}^{a}$ *vs.* THE SATURATED CALOMEL ELECTRODE

Substance	*p*H (aq.)	$E_{1/2}{}^{1}$	$E_{1/2}{}^{2}$	$E_{1/2}{}^{12}$	$E_{1/2}{}^{3}$
Benzaldehyde	2.2	1.01h	...		
	3.0	1.06h	1.34h		
	5.0	...	...	1.27f	
	12.0	...	...	1.48h	...
	12.0^{b}	...	...	1.69f	
	12.0^{f}	...	...	1.43h	1.75h
p-Hydroxybenzaldehyde	2.2	1.11h	...		
	5.5	1.28h	1.54h		
	6.5	...	...	1.48f	
	11.0	...	...	1.74h	...
	12.0^{b}	...	...	1.72h	1.86h
Salicylaldehyde	2.2	1.03h	...		
	4.0	1.16h	1.29h		
	5.3	...	...	1.28f	
	12.0	...	...	1.69h	...
	12.0^{b}	...	...	1.66f	
	10.0^{c}	...	...	1.53h	1.69h
p-Methoxybenzaldehyde	2.2	1.05h	...		
	4.4	1.19h	1.38h		
	5.5	...	...	1.32f	
	12.0	...	...	1.55h	...
	12.0^{b}	...	...	1.57h	1.86h
o-Methoxybenzaldehyde	2.2	0.95h	...		
	3.3	1.01h	1.28h		
	6.1	...	...	1.25f	
	12.0	...	...	1.45h	...
	12.0^{d}	...	...	1.47h	1.93h
Piperonal	2.5	1.03h	...		
	4.0	1.13h	1.35h		
	5.9	...	...	1.32f	
	12.0	...	...	1.54h	...
	12.0^{b}	...	...	1.54h	1.82h
Vanillin	2.4	1.07h	...		
	4.8	1.23h	1.38h		
	5.8	...	...	1.35f	
	11.3	...	...	1.74h	...
	12.0^{b}	...	...	1.71h	1.83h
p-Dimethylaminobenzaldehyde	2.0	0.90h	...		
	7.5	1.35h	1.55h		
	8.9	...	...	1.57f	
	12.0	...	...	1.65h	...
	12.0^{b}	...	...	1.63h	1.86h
1-Naphthaldehyde	2.2	0.90h	...		
	3.4	0.96h	1.16h		
	7.0	...	...	1.23f	
	12.0	...	...	1.32h	
	12.0^{g}	...	...	1.29^{e}	1.62^{e}
2-Naphthaldehyde	2.2	0.93h	...		
	3.1	0.99h	1.27h		
	6.0	...	...	1.25f	
	12.0	...	...	1.41h	...
	12.0^{f}	...	...	1.38h	1.71h
9-Phenanthraldehyde	2.2	0.86h	...		
	3.0	0.91h	1.25h		
	7.0	...	...	1.22f	
	12.0	...	...	1.32h	...
	12.0^{f}	...	...	1.29^{g}	1.62^{g}

[a] All $E_{1/2}$ values are negative. The letters *h* and *f* following $E_{1/2}$ values indicate that the current was half (one electron) or full value (two electrons). Values of i_D/C were normally 3.8 to 4.5 for full current, 1.8 to 2.2 for half-current. [b] Results obtained in a calcium hydroxide–calcium chloride buffer (ref. 13). [c] Carbonate buffer plus 0.05 *M* *t*-butylammonium chloride. [d] 0.01 *M* tetramethylammonium hydroxide. [e] The height of the first wave was about three times that of the second. [f] Concentration of calcium chloride in buffer 0.05 *M* instead of 0.1 *M*. [g] The height of the first wave was about 1.4 times that of the second.

It is obvious that any general mechanism for the reduction of carbonyl compounds should account for the differences shown by various ketones and aldehydes as regards the separation of waves 1–2 and 3 in alkaline media. For example, the wave shown by a ketone, such as benzophenone, may be a single one of full height (two electrons), whereas that shown by benzaldehyde under identical environmental conditions is only half-height. At the same time, waves 1–2 and 3 shown by another ketone, such as fluorenone, under the same conditions may be completely separate. A qualitative correlation between the molecular structure and the separation of waves (or decrease in wave height) in alkaline media has been pointed out in the case of a number of aromatic ketones, furfural and benzaldehyde.[10,14,19–21] This correlation has been based upon the effect of structure on the position of the dimerization equilibrium postulated by Ashworth. It should be noted, however, that this interpretation does not require a metal ketyl intermediate *per se*, but is based on the assumption that the intermediate, be it metal ketyl, carbinol-free radical

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[17] P. J. Elving, private communication. It should be noted that the carbinolate free radical ion is the anion of the metal ketyl.

[18] These authors write the two structures $RCH_2\text{–}O$ and $RCH\text{–}OH$ as mesomeric forms of the carbinol-free radical, where actually they are tautomers.

[19] R. A. Day, Jr., and R. E. Biggers, THIS JOURNAL, **75**, 738 (1953).

[20] R. A. Day, Jr., and W. A. Blanchard, *ibid.*, **76**, 1166 (1954).

[21] This correlation also holds for aliphatic ketones, as will be reported in a later article.

or carbinolate-free radical ion, is in reversible equilibrium with the dimer. It also should be emphasized that the equilibrium is assumed to exist only at the electrode surface. Dimerization in the body of the solution is known to be irreversible in aqueous media and the dimer is the product of electrolysis (see Experimental section). It has been found that waves 1–2 and 3 have a greater tendency to be separate when the carbonyl compound contains groups known to have the least tendency to stabilize a free radical, and hence to promote dimerization.

The above assumption readily accounts for the decrease to half-height of wave 1–2 (that is, the separation of wave 3) of aromatic aldehydes in alkaline media, where many aromatic ketones exhibit only a single two-electron wave. The free radical intermediate formed from benzaldehyde is expected to dimerize much more strongly than the corresponding radical formed, for example, from an aromatic ketone, such as benzophenone. The latter molecule contains two phenyl groups, whereas the former contains only one, plus a hydrogen atom. From both resonance and steric considerations[22] the monomeric intermediate produced from the ketone should be more stable relative to the dimer than the monomeric form produced from the aldehyde. The equilibrium assumed above should greatly favor the dimer in the case of the aldehyde and hence the potential needed to produce wave 3 is much higher than the potential required to produce the intermediate. It is logical that the dimer (pinacol) is the product of electrolysis of aromatic aldehydes in 0.01 M sodium hydroxide where the wave is half-height. We have confirmed this (see Experimental section) by the large-scale electrolysis of 2-naphthaldehyde in 0.01 M sodium hydroxide. The dimer 1,2-di-β-naphthyl-1,2-ethanediol was isolated in good yield and the coulometric measurement indicated that one electron per molecule was consumed in the reduction process. The dimer also has been isolated under similar conditions in the case of benzaldehyde.[7] On the other hand, the secondary alcohol, β-naphthylcarbinol, is the product of electrolysis under conditions (in the presence of calcium) such that wave 3 is observed. Coulometric measurement showed that two electrons were consumed per molecule of aldehyde in this case.

It was of particular interest to note the effect of the substituents in the benzene nucleus on the position of wave 3 of these aldehydes. Seven of the molecules studied contain as substituents the hydroxy, methoxy and dimethylamino groups which can release electrons to the benzene ring. The electron density of the benzene ring is hence greater relative to the unsubstituted ring, and presumably this effect should decrease the stability of the monomeric intermediate and favor the formation of the dimer.[23] It will be noted from Table I that wave 3 for all these aldehydes except salicylaldehyde occurs at slightly more negative potentials than that of benzaldehyde. In other words, wave 1–2 and wave 3 are more inclined to be separate than in the case of the unsubstituted molecule. Actually in the same buffer of calcium hydroxide and calcium chloride the two waves of benzaldehyde (and salicylaldehyde) are merged, whereas they are separated in the case of the other aldehydes. Wave 3 can be observed separate from wave 1–2 for benzaldehyde and salicylaldehyde by working at a lower concentration of calcium ion. These results indicate that the effect of these substituents in the aromatic nucleus is to increase (compared to benzaldehyde) the extent of dimerization of the intermediate. They also indicate that dimerization is not as great in the case of salicylaldehyde as that of the others. This observation is not unreasonable in light of the fact that dimerization in this instance brings into close proximity the two negatively charged groups substituted in the positions *ortho* to the carbonyl.

The 1- and 2-naphthyl and 9-phenanthryl groups are known to stabilize a free radical to a greater extent than a phenyl group.[22] It will be noted from Table I that wave 3 of these aldehydes occurs at more positive potentials than that of benzaldehyde. It also was found that waves 1–2 and 3 are more readily merged by calcium ions than is the case with the other aromatic aldehydes. This behavior indicates that the intermediates produced from these three aldehydes do not dimerize as readily as those produced from the other aldehydes. In fact, it appears that the 1-naphthyl group stabilizes the monomer to a greater extent than does the 2-naphthyl group, as should be the case,[22] but the difference is undoubtedly small. 1-Naphthaldehyde actually resembles the ketone benzophenone in its tendency to form one large and one small wave in certain basic media.

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[22] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, p. 146.

[23] The p-chlorophenyl group has been reported to have less tendency than a phenyl group to stabilize a free radical of the triphenylmethyl type (see H. Gilman, "Organic Chemistry, An Advanced Treatise," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 591). The ketone p-chlorobenzophenone has been found to form separate waves more readily than benzophenone, in agreement with the above postulate (see ref. 19). However, the methoxy group in the o- or p-position has been reported to have a greater tendency to stabilize a free radical than the phenyl group. Some of this earlier work was later repeated and lower percentage dissociations found, but that on the methoxy compound was not repeated.