Polarographic Reductions of Some Carbonyl Compounds

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The complete reduction scheme for aryl alkyl ketones can be elucidated only by studying several series of compounds. The effect of protonation by acids other than hydroxonium ion on the antecedent reaction and the effect of alkali metal cations on the protonation of radical anions are discussed. Effects of substituents in α- and β-positions in the side chain and on the phenyl ring are compared. Effects of electron-accepting substituents indicate increased conjugation in the transition state. Reduction of α,β-unsaturated aldehydes and ketones produces in the first two-electron step the saturated aldehydes or ketones. Proton transfers in various pH-ranges were elucidated and the role of chemical transformations in the reduction of α,β-unsaturated aldehydes and ketones is manifested by a formation of a separate wave. In the study of saturated aldehydes the structural effects on the dehydration reaction were compared. The acid-base reaction that causes with some aldehydes a decrease in the reduction current at high pH was attributed to the formation of the dianion of the hydrated form or more probably to the carbanion formation rather than to the monoanion. This was deduced from the study of the u.-v. spectra, in which the band at 280-300 mμ with ε of the order 10^3 was attributed to the carbanion.

The polarographic method has proved useful for the studying of the course of the electrolytic processes occurring during the electroreduction of various carbonyl compounds in the protic media. By changing the composition of the supporting electrolyte, in particular the acidity and the kind and concentration of the cations present, it is possible to obtain information on antecedent and interposed chemical reactions, accompanying the electrode process proper. To identify the individual steps in the electrode process it proved necessary to carry out investigations on various types of compounds. Not only was it necessary to study separately aldehydes and ketones and compare aliphatic, aromatic and unsaturated compounds only among themselves, but even inside such narrowly selected groups—e.g., aliphatic aldehydes or alkyl aryl ketones—it proved necessary to study several types of compounds. In most groups investigated, a study, even a detailed one, of one single compound cannot reveal all the information on the individual steps involved. This is because, depending upon the structure of the compound studied, some steps become more important and some less important. Moreover, with certain compounds some reaction steps cannot be followed due to interferences, which can be caused, e.g., by the coalescence of one of the waves with the current due to the supporting electrolyte, or by an overlapping of waves corresponding to consecutive processes. With some compounds it was possible to obtain detailed information about the individual steps of the electrode process in acid media but it was impossible to obtain more than general information about the processes at higher pH. On the other hand, with other types of compounds it was possible to acquire a detailed insight into the processes in alkaline media but not in acid. So far, no single compound has been found that would provide data which allows one to interpret all of the details over the whole range of conditions

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investigated.   Another example, indicating the importance of investigation carried out with a wide range of structurally different compounds, and the selection of a proper type of substance for a study of an individual step in the electrode process, is the study of the effects of cations present in the supporting electrolyte on the wave-heights in alkaline media.   With simple aryl alkyl ketones and benzaldehydes, where this effect was first observed,[1] the current corresponding to the reduction of a species formed by interaction of a radical anion with the cation of the supporting electrolyte cannot be distinguished from the current due to the reduction of the protonized form of the product of the one-electron reduction (i.e., the radical).   When the effect of the nature of the cation and concentration was studied with α,β-unsaturated aldehydes or ketones, the waves corresponding to the reduction of the radical and those to the reduction of the product of interaction of the radical anion with the cation are well separated and hence far more suitable for quantitative investigation than are aryl alkyl ketones or benzaldehydes.

This situation explains why even when the course of the polarographic reduction of aldehydes and ketones has been studied extensively,[1-32] there still remained individual steps in the electrode process that were missed or misinterpreted.   In most investigations, attention has been paid only to a certain aspect of the problem. Either the study was restricted to a certain—acid or alkaline—pH-range, or the stress was laid on detailed examination of the effects of concentration of the electroactive compounds, cations or solvents, or the investigation was carried out only for a small group of compounds, or attention was limited to a comparison of half-wave potentials.

In our studies carbonyl compounds having a wide variation in the structure have been compared in order to elucidate some of the individual steps in the electrode process so that a general scheme for the reduction process can be proposed.

EXPERIMENTAL

Polarographic current-voltage curves were recorded with dropping mercury electrodes with droptimes of about 3 sec in 1 mKCl at 0·0 V and outflow velocities of about 2 mg/sec. Electrolytic cells with reference electrodes separated by liquid junction were used.   The number of electrons transferred was determined by millicoulometry and by comparison with equimolar solutions of depolarizers with well-known electrode processes.   To identify the electrolysis product controlled potential electrolysis was carried out with a dropping mercury electrode in small volumes (0·5-1·0 ml).   When successive reductions took place and polarographic curves showed two or more waves, the more negative waves were compared with the waves obtained in solutions containing the assumed product (of the first reduction process) only.

Identification of controlled potential electrolysis products was carried out using polarography, u.v. spectra, paper and thin layer chromatography, gas-liquid chromatography, in particular in combination with the flame-ionization detector, determination of pK-values and colour reactions (spot tests).

Determination of yields of controlled potential electrolysis products was carried out by polarography, spectrophotometry or submicrotitrations.   Organo mercury compounds were determined by atomic absorption and using an instrument for determining the mercury vapour pressure.

For identification of the products at the dropping mercury electrode rectangular voltage polarization (commutator method), oscillographic polarography ($dE/dt = f(E)$) curves and single-sweep methods (cathode-ray polarography) were used.   In some instances the products formed at the dropping mercury electrode were compared with those obtained with a triangular voltage polarization with a hanging mercury drop electrode and with a stirred mercury pool electrode.   Adsorption phenomena were investigated using the a.c polarography, electrocapillary curves, single-sweep methods and $dE/dt = f(E)$ curves.
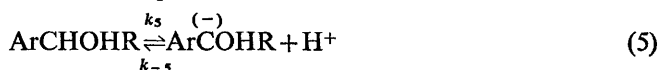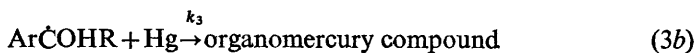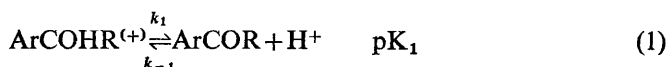
RESULTS AND DISCUSSION

ARYL ALKYL AND DIARYL KETONES

The polarographic behaviour of aryl alkyl ketones is complex and therefore it seemed useful to discuss separately the reduction in acid media, in medium pH-range, and in alkaline solutions and in the intermediate pH-range and the structural effects.

REDUCTION IN ACID MEDIA

In acid media the reduction corresponds essentially to two one-electron processes and waves (i_1 and i_2) at potentials E_1 and E_2 are observed (fig. 1A). The properties of these waves can be explained by scheme (1)-(5), corresponding to a sequence of individual reduction steps proton, electron, electron, proton (H^+, e, e, H^+):

$$ArCOHR^{(+)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ArCOR + H^+ \qquad pK_1 \qquad (1)$$

$$ArCOHR^{(+)} + e \underset{E_1}{\rightleftharpoons} Ar\dot{C}OHR \qquad i_1 \qquad (2)$$

$$2Ar\dot{C}OHR \overset{k_2}{\rightarrow} dimers \qquad (3a)$$

$$Ar\dot{C}OHR + Hg \overset{k_3}{\rightarrow} organomercury\ compound \qquad (3b)$$

$$Ar\dot{C}OHR + solvent \overset{k_4}{\rightarrow} products \qquad (3c)$$

$$Ar\dot{C}OHR + e \overset{(-)}{\underset{E_2}{\rightarrow}} Ar\overset{(-)}{C}OHR \qquad i_2 \qquad (4)$$

$$ArCHOHR \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} Ar\overset{(-)}{C}OHR + H^+ \qquad (5)$$

In agreement with this scheme the controlled potential electrolysis at the potential corresponding to the limiting current of wave i_1 in acid media yields predominantly pinacol. The first wave i_1 corresponds to the reduction of the protonized form.[1, 2] Further support for the above scheme can be found in the shifts of half-wave potentials. Because the electron transfer in step (4) is not preceded by an proton-transfer, the half-wave potential of wave i_2 is practically pH-independent (fig. 1B). On the other hand, the half-wave potential of wave i_1 is shifted with increasing pH to more negative potentials. This is caused by the acid-base equilibria (1) preceding the electron transfer (2). In sufficiently acid media, i.e. at pH < (pK' − 1) (where the value of pK' equals the value of pH at which the wave heights of the protonized and unprotonized form are equal) the establishment of the equilibrium (1) can be considered to be fast. The half-wave potential would become pH-independent at pH < pK_1, but the value of the equilibrium constant pK_1 for most of the studied compounds is well below zero and hence beyond the acidity range normally studied. For some ketones it is assumed that equilibrium (2) at the electrode surface is rapidly established[17, 19, 22, 23] and hence the first electron-uptake is considered to be a reversible process. The shifts of the half-wave potentials of the second one-electron wave i_2 with changes in cation and solvent concentration and kind[19, 20, 22, 26] can be interpreted by the effects of changes in the double-layer composition and adsorption-desorption processes rather than by an adduct formation.

Because of the shift of the first wave i_1 and the practical pH-independence of the half-wave potential of the second wave i_2, (at sufficiently high pH-values) the two

waves i_1 and i_2 can merge into one two-electron wave (i_{1+2}) (fig. 2), if the potential of the wave i_2 is positive enough. The reduction product of the combined two-electron wave (i_{1+2}) is the corresponding alcohol.[3] As the increase in ethanol concentration
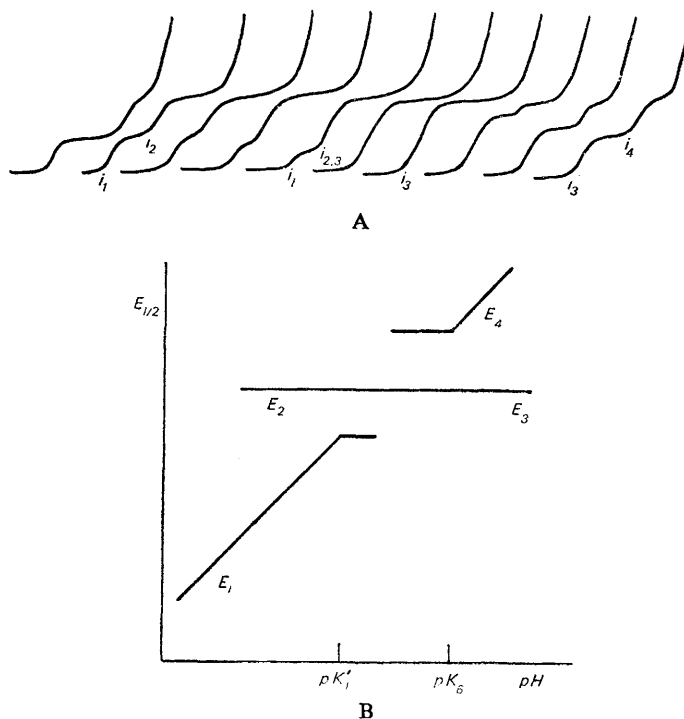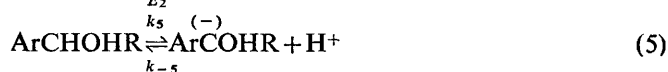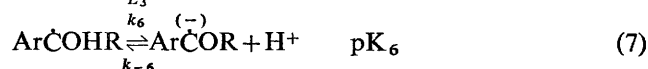

FIG. 1.—pH-Dependence of the reduction waves of aryl alkyl ketones for $E_1 < E_2$ and $E_2 \approx E_3$ A, polarographic i-E curves (schematically, pH increasing from left to right) ; B, half-wave potentials.

results in a shift of the wave i_2 to more negative potentials whereas the half-wave potential of wave i_1 remains practically unaffected,[26] a separation of waves i_1 and i_2 can be oberved at high ethanol concentrations even at such high pH-values, when at low ethanol concentration only one combined wave i_{1+2} is observed.

REDUCTION IN MEDIUM pH-RANGE

In aqueous solutions in the medium pH-range one two-electron wave (i_3 in fig. 1A-3A), is observed. The process can be depicted by the scheme (6), (7), (4), (5) which corresponds to the sequence electron, proton, electron, proton (e, H+, e, H+), under the assumption that the difference between potentials E_2 and E_3 is small or that E_3 is more positive than E_2 :

$$\text{ArCOR} + e \rightarrow \overset{(-)}{\text{Ar\.COR}} \qquad i_3 \qquad (6)$$
$$\underset{E_3}{}$$

$$\overset{k_6}{\underset{k_{-6}}{\text{Ar\.COHR} \rightleftharpoons \overset{(-)}{\text{Ar\.COR}} + \text{H}^+}} \qquad pK_6 \qquad (7)$$

$$\text{Ar\.COHR} + e \rightarrow \overset{(-)}{\text{ArCOHR}} \qquad i_2, i_3 \qquad (4)$$
$$\underset{E_2}{}$$

$$\overset{k_5}{\underset{k_{-5}}{\text{ArCHOHR} \rightleftharpoons \overset{(-)}{\text{ArCOHR}} + \text{H}^+}} \qquad (5)$$

Radical ArĊOHR can undergo reactions $(3a)$-$(3c)$, but because, (a) the value i/c for this wave remains practically independent of concentration, (b) the coulometrically determined number of electrons is two, (c) alcohol was found as the only product of controlled potential electrolysis, these side reactions are probably not fast enough to affect the electrode process.
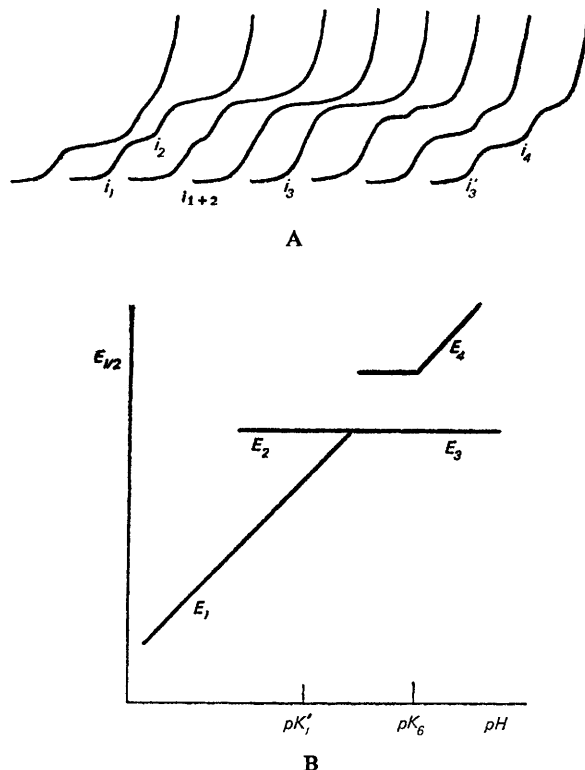

FIG. 2.—pH-Dependence of the reduction waves of aryl alkyl ketones for $E_1 \approx E_2 \approx E_3$ at higher pH-values.   A, polarographic i-E curves (schematically); B, half-wave potentials.

The deduction that the first electron is accepted prior to the first proton is based on the observations that the half-wave potential of the two electron wave i_3 is pratically pH-independent (fig. 1B, 2B).   Such a behaviour can be explained either by assuming that potential-determining step is the first one-electron addition (6), or that the acid-base equilibrium is completely shifted to the left-hand side (i.e., that the experiments are carried out at pH-values considerably smaller than pK_6).   The former explanation is supported by the observation that the logarithmic analysis for a number of aryl ketones in this pH-range corresponds to a one-electron reversible process.

The electrode process follows the scheme (6), (7), (4) and (5) in the medium pH-range, in which the protonation reaction (1) with constant k_{-1} is already so slow that no considerable amount of the protonized form $ArCOHR^{(+)}$ is present.   On the other hand, the pH must not be too high, so that the reaction (7) with constant k_{-6} is still fast enough to convert all of the radical anion $Ar\overset{(-)}{C}OR$ completely into radical ArĊOHR. With most aryl ketones this scheme is followed between pH 6 and 10.

TRANSITION BETWEEN LOW AND MEDIUM pH-VALUES

At pH-range between the acid and medium pH-values (i.e., usually between pH 3 and 7) the reduction of the protonated form $ArCOHR^{(+)}$ following (1) and (2) and that of the unprotonated form ArCOR according to (6) and (7) are in competition. This competition can be observed on polarographic curves in three main ways shown in fig. 1-3, but we shall restrict ourselves to the most frequently encountered type shown in fig. 1.
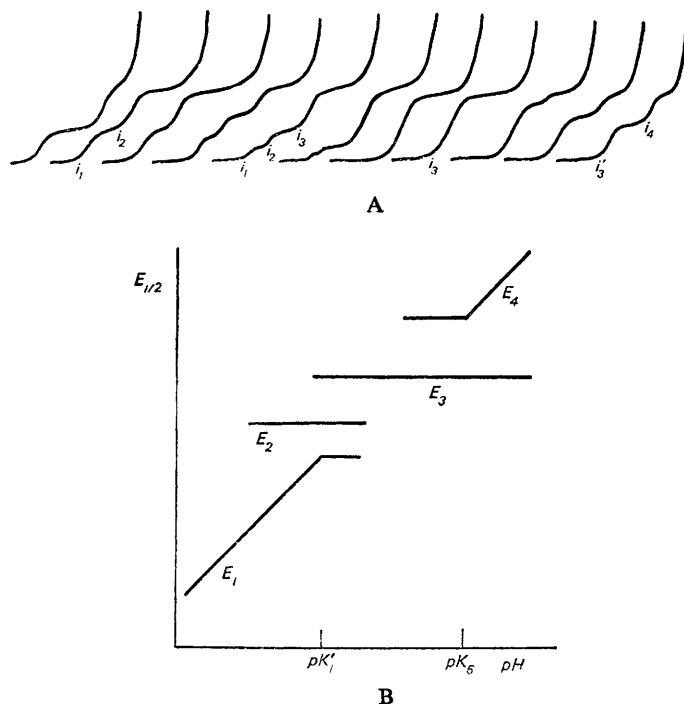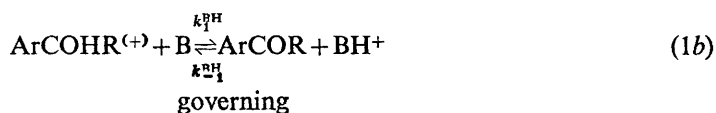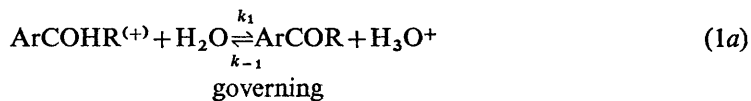

FIG. 3.—pH-Dependence of the reduction waves of aryl alkyl ketones for $E_1 < E_2 < E_3$. A, polarographic i-E curve (schematically); B, half-wave potentials.

In this case the reduction process (2) is preceded by the protonation reaction (1a) in which the establishment of the equilibrium cannot be considered as fastly established. The rate of the protonation with constant k_{-1} governs the height of the wave i_1:

$$ArCOHR^{(+)} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ArCOR + H_3O^+ \tag{1a}$$

governing

$$ArCOHR^{(+)} + B \underset{k_{-1}^{pH}}{\overset{k_1^{pH}}{\rightleftharpoons}} ArCOR + BH^+ \tag{1b}$$

governing

$$ArCOHR^{(+)} + e \underset{E_1}{\rightleftharpoons} Ar\dot{C}OHR \tag{2}$$

In the pH-range in which the rate of protonation with constant k_{-1} decreases and causes the decrease of the current i_1, the waves corresponding to these processes are separated (i.e., $|E_1| < |E_2|$), but simultaneously the waves i_2 and i_3 merge

(i.e., $E_2 \approx E_3$), the first one-electron wave decreases with increasing pH in the form of a dissociation curve. Simultaneously, the wave at the potential E_2 increases until it reaches a height corresponding to the two-electron process and can be represented by the processes (6), (7), (4) and (5). The total height of waves $i_1 + i_2 + i_3$ remains unchanged (fig. 1A). The half-wave potential of the wave i_1 at pH > pK' becomes pH-independent (fig. 1B).

The aryl ketones react not only with hydroxonium ions (1a), but also with other protondonors (1b). This can be proved by the dependence of the wave-height (i_1) on the nature of the acid buffer component, on the concentration of the buffer and from the shape of the i-pH plots. Buffers with constant analytical concentration of buffer components, or with a constant concentration of the acid buffer component give a distorted dissociation curve, in agreement with eqn. (8):

$$\frac{i}{i_d} = \frac{0 \cdot 88(t_1/K_1)^{\frac{1}{2}}[H_3O^+](k_{-1} + k_{-1}^{BH}[BH^+]/[H_3O^+])^{\frac{1}{2}}}{1 + 0 \cdot 88(t_1/K_1)^{\frac{1}{2}}[H_3O^+](k_{-1} + k_{-1}^{BH}[BH^+]/[H_3O^+])^{\frac{1}{2}}}. \tag{8}$$
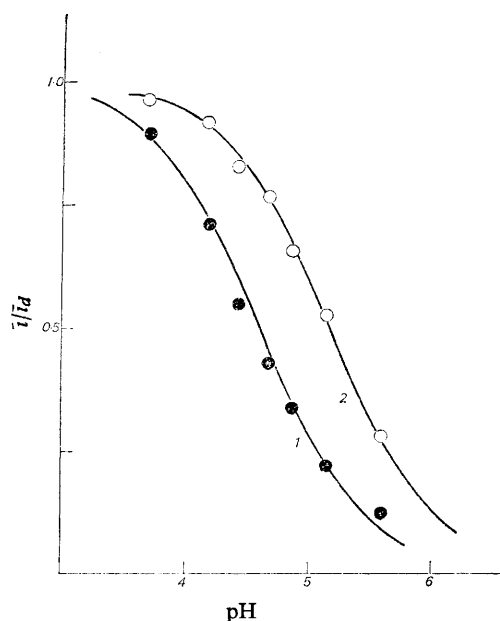

FIG. 4.—pH-Dependence of the ratio $\bar{i}/\bar{i}_d$ for the one-electron wave of n-propyl deoxybenzoin in acetate buffers with sodium acetate concentration constant. Curve 1, 0·05 M sodium acetate; 2, 0·5 M sodium acetate ; theor. curve for pK″ 4·60 (1) and 5·18 (2).

The dependence has the shape of a simple dissociation curve only, when the concentration of the base buffer component is kept constant and then eqn. (9) can be applied :

$$\frac{i}{i_d} = \frac{0 \cdot 88(t_1/K_1)^{\frac{1}{2}}[H_3O^+](k_{-1} + k_{-1}^{BH}[B]/K_{BH})^{\frac{1}{2}}}{1 + 0 \cdot 88(t_1/K_1)^{\frac{1}{2}}[H_3O^+](k_{-1} + k_{-1}^{BH}[B]/K_{BH})^{\frac{1}{2}}}. \tag{9}$$

The inflexion point of such curves, at which $i = i_d/2$ (denoted pK″) depends upon the concentration of the base buffer component [B] and the dissociation curve is shifted towards lower pH-values with decreasing base component concentration (fig. 4). From the dependence of $1/(K″)^2$ on [B] it is possible to evaluate the values of the rate constant for the reaction with the acid buffer component (k_{-1}^{BH}) and with hydrogen ions (k_{-1}).

REDUCTION IN ALKALINE MEDIA

At sufficiently high pH-values, in a medium of ionic strength less than about 0·1 containing only lithium ions, the reduction of aryl ketones takes place in two one-electron steps (i_3' and i_4). The reduction follows scheme (6), (10) and (11) corresponding to the sequence, electron, electron, proton, proton, (e, e, H$^+$, H$^+$):

$$ArCOR + e \rightarrow Ar\overset{(-)}{C}OR \qquad \underset{E_3}{} \qquad i_3' \qquad (6)$$

$$Ar\overset{(-)}{C}OR + e \rightarrow ArCOR^{(2-)} \qquad \underset{E_4}{} \qquad i_4 \qquad (10)$$

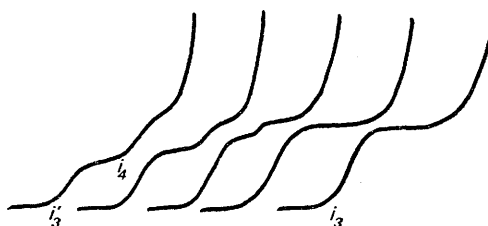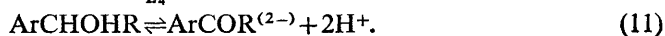$$ArCHOHR \rightleftharpoons ArCOR^{(2-)} + 2H^+. \qquad (11)$$

FIG. 5.—Effect of increasing cation concentration of the reduction waves of aryl alkyl ketones in alkaline media (schematically) $E_5 \approx E_3$.
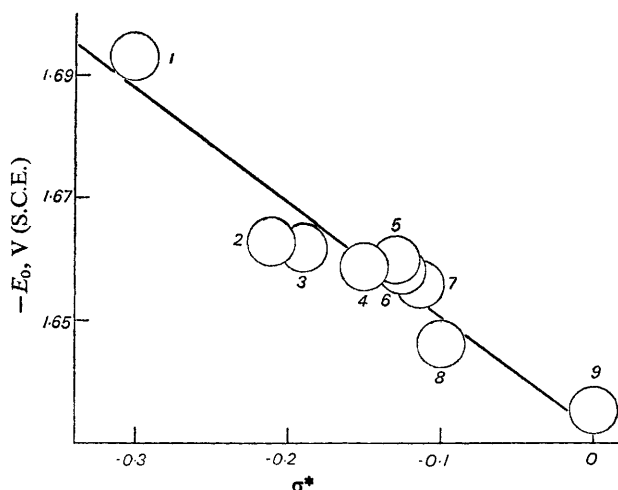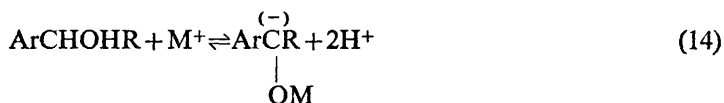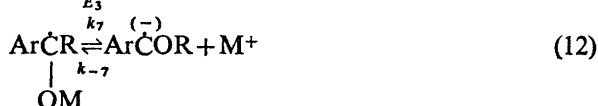

FIG. 6.—Dependence of half-wave potentials of substituted deoxybenzoins of the type $C_6H_5COCH(R)C_6H_5$ in borate buffer pH 9·3 on Taft polar substituent constants σ*. R = (1) tert-C_4H_9; (2) sec-C_4H_9; (3) i-C_3H_7; (4) C_5H_{11}; (5) C_4H_9; (6) i-C_4H_9; (7) C_3H_7; (8) C_2H_5; (9) CH_3; $\rho_\pi^* = 0.18$ V.

In agreement with this scheme the half-wave potentials of wave i_3' and i_4 are practically pH-independent. The scheme is operating at such high pH-values that the rate of protonation of the radical anion (7) with rate constant k_{-6} is negligible. Waves i_3' and i_4 are usually well separated, because the reduction of the radical anion $Ar\overset{(-)}{C}OR$ occurs at more negative potentials than that of the radical $Ar\overset{\cdot}{C}OHR$ (which takes place at the same potential as the unprotonized ketone ArCOR). The potential E_4 can sometimes be so negative that wave i_4 can be overlapped by the current of

the supporting electrolyte. A similar course of reduction has been proposed for the reductions in non-aqueous media.[15] Whereas the waves in alkaline media are little affected by the pH, they depend on the kind and concentration of the cations present in the supporting electrolyte, which affect the half-wave potentials of wave i_4 and the height of wave i_3. The shifts of the wave i_4 (the reduction of the radical anion $Ar\overset{(-)}{\overset{|}{C}}OR$) with concentration of the cations are probably due to double-layer effects.

An increase in the concentration of cations in the supporting electrolyte resulting either from the addition of neutral salt [1, 4, 9] or from an increase in the hydroxide concentration causes the current i_3 to increase (fig. 5). This increase is the greater the larger is the radius of the cation. This is interpreted by a scheme (6), (12), (13) and (14):
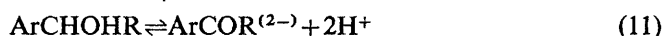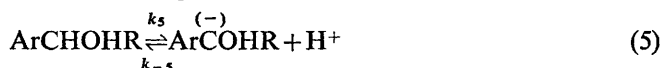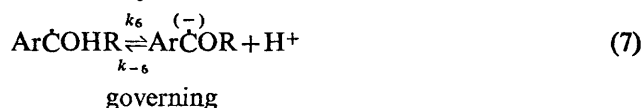
$$ArCOR + e \underset{E_3}{\rightarrow} Ar\overset{(-)}{\overset{|}{C}}OR \qquad\qquad i_3 \qquad\qquad (6)$$

$$\underset{OM}{\overset{k_7}{\underset{k_{-7}}{\rightleftharpoons}}}\ Ar\overset{(-)}{\overset{|}{C}}OR + M^+ \qquad\qquad (12)$$

$$\underset{OM}{Ar\overset{|}{\overset{.}{C}}R} + e \underset{E_5}{\rightarrow} \underset{OM}{Ar\overset{(-)}{\overset{|}{C}}R} \qquad\qquad i_3 \qquad\qquad (13)$$

$$ArCHOHR + M^+ \rightleftharpoons \underset{OM}{Ar\overset{(-)}{\overset{|}{C}}R} + 2H^+ \qquad\qquad (14)$$

The potential E_5 is always more positive than E_4, but in the most cases it is approximately equal to E_3, therefore only an increase of the wave i_3 and not a formation of a new wave is observed. The increase of the wave i_3 is limited by the rate of reaction (12) with rate constant k_{-7}, the total wave-height $i_3 + i_4$ remaining unchanged when a correction is carried out for the changes in viscosity (fig. 5). The product reduced in wave i_3 at sufficiently high pH causes an increase of this wave above the height corresponding to a one-electron process and results from the interaction (12) between the radical anion $Ar\overset{(-)}{\overset{|}{C}}OR$ and cation M^+. The structure of this product, i.e., whether it is a covalent bond and between which atoms it is formed, whether the structure more resembles a complex, a charge-transfer complex or an ion-pair, was not elucidated. The symbol $Ar\overset{|}{\overset{.}{\underset{OM}{C}}}R$ used in eqn. (12)-(14) is used only for convenience.

TRANSITION BETWEEN MEDIUM AND HIGH pH-VALUES

In the intermediate pH-range between the medium and alkaline region (i.e., usually between pH 9 and 12) the rate of protonation reaction (7) with rate constant k_{-6} is no longer fast enough to transform the radical anion $Ar\overset{(-)}{\overset{|}{C}}OR$ completely into the radical $Ar\overset{.}{C}OHR$. In this pH-range, the course (7), (4) and (5) can compete with the course (10) and (11). The height of wave i_3 decreases with increasing pH in the form of a dissociation curve from a height corresponding to a two-electron process to a height corresponding to a one-electron process (fig. 1A-3A). The total height of the currents $i_3 + i_4$ remains unchanged.

In the scheme (6), (7), (4), (5), (10) and (11):

$$\text{ArCOR} + e \rightarrow \overset{(-)}{\text{Ar}\overset{\cdot}{\text{C}}\text{OR}} \qquad (6)$$
$$\underset{E_3}{}$$

$$\underset{k_{-6}}{\overset{k_6}{\text{Ar}\overset{\cdot}{\text{C}}\text{OHR} \rightleftharpoons \overset{(-)}{\text{Ar}\overset{\cdot}{\text{C}}\text{OR}} + \text{H}^+}} \qquad (7)$$

governing

$$\text{Ar}\overset{\cdot}{\text{C}}\text{OHR} + e \rightarrow \overset{(-)}{\text{Ar}\overset{\cdot}{\text{C}}\text{OHR}} \qquad (4)$$
$$\underset{E_2}{}$$

$$\underset{k_{-5}}{\overset{k_5}{\text{ArCHOHR} \rightleftharpoons \overset{(-)}{\text{Ar}\overset{\cdot}{\text{C}}\text{OHR}} + \text{H}^+}} \qquad (5)$$

$$\overset{(-)}{\text{Ar}\overset{\cdot}{\text{C}}\text{OR}} + e \rightarrow \text{ArCOR}^{(2-)} \qquad (10)$$
$$\underset{E_4}{}$$

$$\text{ArCHOHR} \rightleftharpoons \text{ArCOR}^{(2-)} + 2\text{H}^+ \qquad (11)$$

potentials E_3 and E_2 are practically identical and the rate of the interposed reaction (7) governs the height of the first wave i_3 according to the eqn. (15) [34] :

$$\frac{i_3}{i_d} = 1 + \frac{0.886(k_{-6}t_1/K_6)^{\frac{1}{2}}[\text{H}^+]}{1 + 0.886(k_{-6}t_1/K_6)^{\frac{1}{2}}[\text{H}^+]}. \qquad (15)$$

The half-wave potential of wave i_3 is practically pH-independent; the half-wave potential of wave i_4 is independent up to pH = pK_6. At higher pH-values i_4 shifts towards more negative potentials are observed (fig. 1B-3B). Under such condition, reaction (7) is a dissociation equilibrium, preceding the electrode process (10). Because these shifts can be observed only in strongly alkaline media, it is not easy to separate them from the shifts resulting from specific cation effects.

EFFECT OF SUBSTITUENTS IN α-POSITION IN THE SIDE CHAIN

The group of compounds ArCOCHR^{1}R^2 was studied and their behaviour, in particular their half-wave potentials, were compared. Marked steric effects were observed for compounds with branched chains, where all the substituents were alkyl groups (R^1 = R^2 = alkyl). These effects were detected by deviations from linear free energy plots ($E_{\frac{1}{2}} - \sigma^*$) or half-wave potentials with R being bulky alkyl groups and from the non-additivity of substituent effects. It is assumed that these steric effects result from bulky groups preventing an optimum orientation of the ketone ArCOCHR^{1}R^2 at the electrode surface.

On the other hand for alkyl substituted deoxybenzoin (R^1 = phenyl, R^2 = alkyl)[35] including the tert butyl derivative, a decrease in the values $RT/\alpha nF$ with increasing negative value of the Taft substituent constant σ_R^* and a good linear $E_{\frac{1}{2}} - \sigma^*$ correlation was found (fig. 6). This indicates that the polar effect of the alkyl groups predominates. It can be assumed that both phenyl rings are oriented (probably flat) to the surface of the electrode in such a way that the orientation of the carbonyl group is fixed and unaffected by the presence even of bulky alkyl groups, which are forced into a position away from the electrode surface, enabling rear attack of the carbonyl carbon in the reduction process. If the adsorbed phenyl rings are in a trans-position, and if the transfer of the second proton (which joins the carbon) takes place before the molecule leaves its orientation at the surface, the observed yield of the erythro-epimer [10] can be explained.

In the reduction of aminoketones [36] (R^1 = H or alkyl, R^2 = NR$_2$ or NR$_3^{(+)}$) the C—N bond is cleaved prior to the reduction of the carbonyl group; similarly in the reduction of phenacyl sulphonium ions [37] (R^1 = H, R^2 = SR$^{(+)}$) the C—S bond

is cleaved first.   The leaving groups are NHR_2, NR_3 or SR_2 ; to the resulting carbanion seemingly the enolate canonical form has an important contribution and the rate of its transformation into ketone limits the height of the ketone wave.

EFFECT OF SUBSTITUENTS IN β-POSITION IN THE SIDE CHAIN

In the group of compounds $ArCOCH_2CHR^1R^2$ the effect of R = phenyl in dihydrochalcone on the reduction when compared with propiophenone (R = H) was relatively weak.   The reduction takes place in a potential region where the ketone can be considered to be desorbed.   The desorption was proved from the change of the capacity current, a.c. polarography, electrocapillary curves (measured using the electrocapillary electrometer and the drop-time) and from $dE/dt = f(E)$ curves.

The reduction of β-ketosulphides [38] (R^1 = SR, R^2 = phenyl) follows a path (1)-(7) and (10)-(14) similar to unsubstituted ketones and the polarographic curves follow the pattern shown in fig. 1A, with the exception that the potential E_4 was too negative and wave i_4 does not appear before the reduction of the supporting electrolyte. This indicates protonation of the carbonyl group and makes β-ketosulphides different from β-aminoketones, [39] for which the protonation takes place preferentially at the amino group.   For β-aminoketones (R^1 = H, R^2 = NR_2) over the entire pH-range studied the electrolysis can be attributed to the reduction of the unprotonated carbonyl group.   In accordance with this interpretation, only one two-electron wave was observed over the range from pH 2 to 11 (at pH > 10 the measurements were made at lower temperature to prevent the effect of elimination).   The shifts of half-wave potentials observed for β-aminoketones can be ascribed to the proton transfer on the amino nitrogen.

An alternative explanation, viz., that the amino compounds are favourably oriented at the electrode surface so that a simultaneous two-electron uptake or two consecutive one-electron processes at the same potential are possible, cannot be excluded.   Since for sulphur compounds there is to be expected a greater affinity towards mercury than for amino compounds, the latter explanation seems less probable.

The effects of alkyl and aryl groups R bound to the heteroatom SR and NR_2 were treated using the Taft polar substituent constants σ_R^* in the linear free energy relationship $\Delta E_{\frac{1}{2}} = \rho_\pi^* \sigma_R^*$.   Phenyl and benzyl derivatives show deviations attributed to mesomeric effects and branched alkyl derivatives deviations ascribed to steric effects. It was found that for the one-electron wave in the reduction of the protonized carbonyl of β-ketosulphides in acid media, a reaction constant $\rho_{\pi, t_1}^* = -0.21$ V and for the two-electron wave of the unprotonized carbonyl in medium pH-range $\rho_{\pi, t_3}^* = +0.09$ V indicates a difference in mechanism.   For the observed two-electron process of β-aminoketones (R^1 = H, R^2 = NR_2) with unbranched alkyl group R the value of the reaction constant $\rho_\pi^* = -1.82$ V.

EFFECT OF SUBSTITUENTS ON THE PHENYL RING

The effects of substituents on the half-wave potentials of m- and p-substituted benzophenones were studied [40] for the one-electron wave corresponding to processes (1)-(3) in acidic media, for the two-electron wave corresponding to the scheme (6), (7), (4) and (5) in the medium pH-range and in 0.1 M sodium hydroxide corresponding predominantly to the one-electron process (6), (10), and (11), even when the wave-height can be affected by processes (12)-(14).   All the half-wave potentials have shown a reasonable correlation with Hammett substituent constants according to eqn. (16) (fig. 7):

$$\Delta E_{\frac{1}{2}} = \rho_\pi \sigma_{x}. \qquad (16)$$

This indicates that half-wave potentials are controlled by substituent I and M effects transmitted through the benzene nucleus. The reaction constants (table 1) have a sign expected for a nucleophilic attack by an electron, their absolute values are of an order of magnitude generally found [41] and increase with increasing negative value
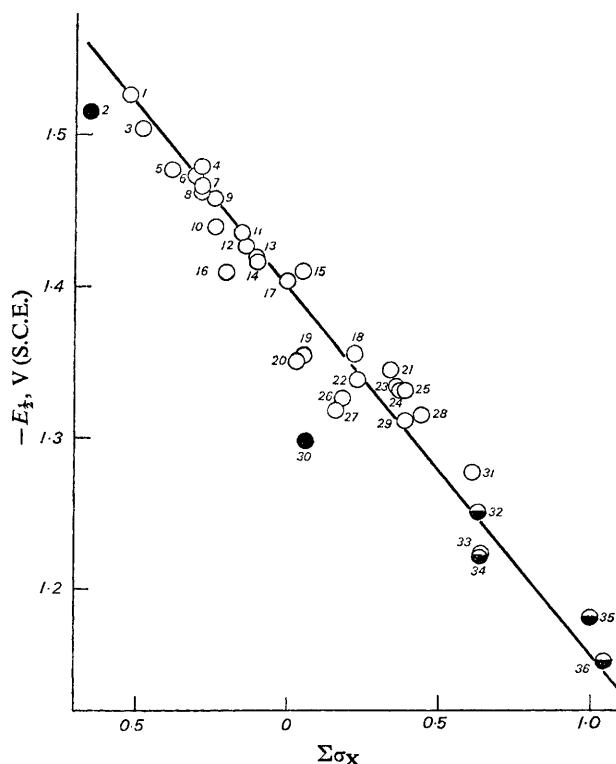

FIG. 7.—Dependence of half-wave potentials of substituted benzophenones in borate buffer pH 9·3 on the sum of Hammett substituent constants $\Sigma\sigma_X$. (1) 4,4(OCH$_3$)$_2$; (2) 4-NH$_2$; (3) 3,4,3',4'(CH$_3$)$_4$; (4) 3,4,3',4'(OCH$_3$)$_4$; (5) 4,4'(tC$_4$H$_9$)$_2$; (6) 4,4'(iC$_3$H$_7$)$_2$; (7) 4,4'(C$_2$H$_5$)$_2$; (8) 4,4'(CH$_3$)$_2$; (9) 3,4'(CH$_3$)$_2$; (10) 3,4'(CH$_3$)$_2$; (11) 4-iC$_3$H$_7$; (12) 4-CH$_3$; (13) 3-COO$^-$; (14) 3-CH$_3$; (15) 4-F; (16) 3,5(CH$_3$)$_2$; (17) H; (18) 4-Cl; (19) 3-CH$_2$OC$_6$H$_5$; (20) 4-C$_6$H$_5$; (21) 3-F; (22) 4-Br; (23) 3-COOCH$_3$; (24) 3-CONH$_2$; (25) 3-Cl; (26) 4-CH$_2$CN; (27) 3-CH$_2$CN; (28) 4,4'(Cl)$_2$; (29) 3-Br; (30) 3-CH$_2$OC$_6$H$_5$; (31) 3-CN; (32) 4-CONH$_2$; (33) 3-SO$_2$CH$_3$; (34) 4-COOCH$_3$; (35) 4-CN; (36) 4-SO$_2$CH$_3$. Full points deviate; halved points $\sigma\overline{x}$; $\rho_\pi = 0\cdot25$ V.

TABLE 1.—REACTION CONSTANTS (ρ_π) AND HALF-WAVE POTENTIALS OF UNSUBSTITUTED BENZO-PHENONE $(E_{\frac{1}{2}})_H$

media	ρ_π (V)	$(E_{\frac{1}{2}})_H$ (V) (S.C.E.)
0·1 M HCl	0·15	−0·86
borax, pH 9·3	0·25	−1·40$_4$
0·1 M NaOH	0·26	−1·49$_7$

of the half-wave potential of the unsubstituted parent compound (table 1). The values are practically identical in borax and in sodium hydroxide indicating that the potential determining step might be the same, probably reaction (6).

For acceptor groups σ^-_{p-x} rather than σ_{p-x} must be used in eqn. (16), as is used for half-wave potentials in some other reaction series.[41] Because the reactive grouping

and the substituent are of the same type, conjugation interaction between these two groups in the ground state cannot be offered as an explanation for the application of constants σ_{p-x}^-. A conjugation in the transition state, due to the increased relative contribution of structures C and D (in addition to the structure A to which the greatest contribution can be attributed) in the presence of an acceptor group X, can explain the observed shifts of half-wave potentials to more positive values.[40]
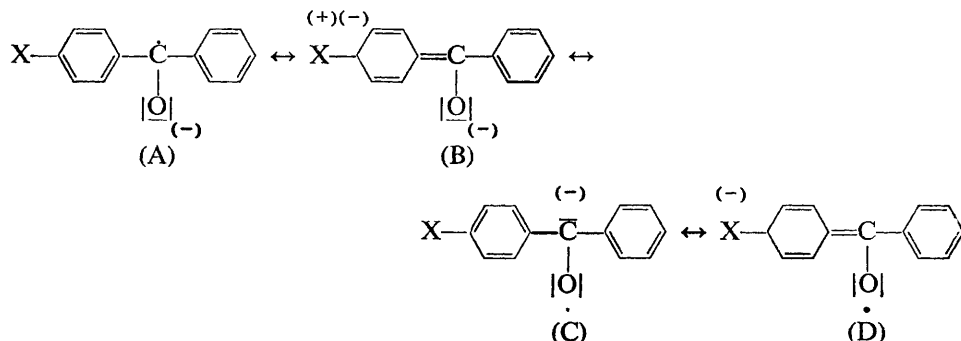
For an understanding of organic electrode processes the observation of deviations from linear $E_{\frac{1}{2}} - \sigma_X$ and similar plots is of even greater importance than the existence of a linear relationship. In the benzophenone series the deviation of the half-wave potential of 4-cyanobenzophenone in acidic media lead to detection of the reducibility of the protonated cyano group in 4-cyanobenzophenone and other substituted benzonitriles.[42]

Application of eqn. (17) derived by Exner [43]

$$\Delta(E_{\frac{1}{2}})_{p-X} = 1\cdot14\Delta(E_{\frac{1}{2}})_{m-X} \tag{17}$$

is possible only for substituents without a free electron pair in the α-position. Significant deviations for acceptor substituents further indicates their conjugative participation with the reaction centre in the transition state.

α,β-UNSATURATED ALDEHYDES AND KETONES

Among the α,β-unsaturated aldehydes and ketones of the general formula $R^1COCH=CHR^2$ examined, cinnamaldehyde [44] ($R^1 = H$, $R^2 = C_6H_5$), phenyl vinyl ketone [45] ($R^1 = C_6H_5$, $R^2 = H$) and chalkone [46, 47] ($R^1 = R^2 = C_6H_5$) were studied in some detail. These systems have in common that in the first, two-electron step (i_I) the double bond is reduced and this process (which can be step-wise) is followed by the reduction (i_{II}) of the saturated carbonyl compound so formed. Such a sequence was recognized early for ketones,[2] but not for aldehydes. For cinnamaldehyde even recently [48] the reduction of the aldehydic group was considered to precede the reduction of the double bond. The saturated carbonyl compound to be reduced in the second step must undergo either enolate-ketone transformation [45] for ketones or dehydration of the carbonyl group for aldehydes.

For a general description of individual steps (fig. 8 and 9) it seems to be useful to divide the whole pH-range into four separate ranges: range I corresponds to acid media, usually below pH 4, in which both the groupings, $CH=CHCO$ and CH_2CH_2CO, are reduced in their protonated forms. In range II, usually between pH 5 and 7, the double bond is reduced in the protonated form of $CH=CHCO$, but the carbonyl in the unprotonated form of CH_2CH_2CO. In the narrow range III,

usually at pH 8-9, both $CH{=}CHCO$ and CH_2CH_2CO are reduced in unprotonated forms, in two-electron steps. In range IV, usually above pH 11 or 12, the reduction of the unprotonated form of $CH{=}CHCO$ takes place in two one-electron steps.
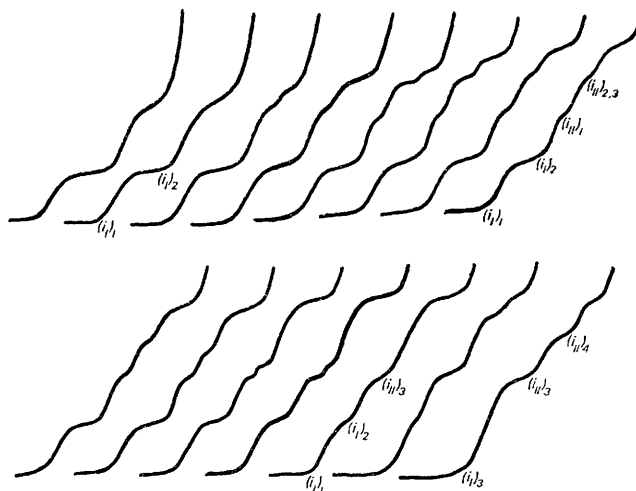

FIG. 8.—pH Dependence of the reduction waves of α, β-unsaturated ketones (schematically, pH increasing from left to right).
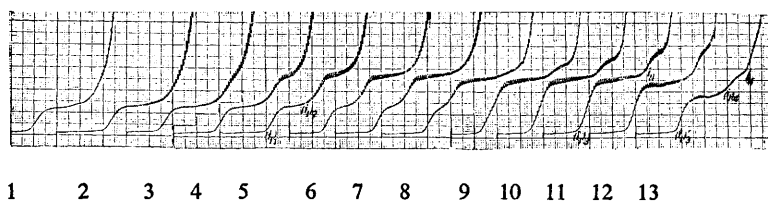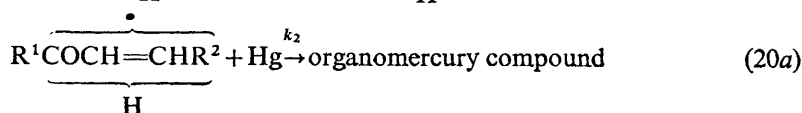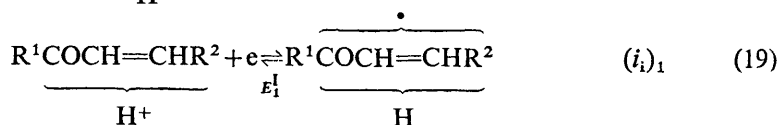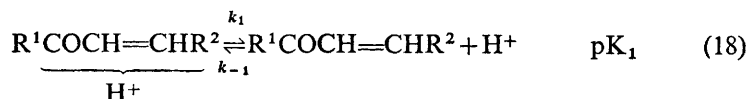

1   2   3   4   5   6   7   8   9   10   11   12   13

FIG. 9.—Dependence of the reduction waves of cinnamaldehyde on pH. 2×10^{-4} M cinnamaldehyde in Britton Robinson buffers containing 25 % ethanol. pH values 1, 2·3; 2, 2·7; 3, 3·55; 4, 4·6; 5, 5·3; 6, 6·5; 7, 7·0; 8, 7·7; 9, 8·85; 10, 9·5; 11, 9·9; 12, 10·4; 13, 11·8. Curves starting at 1, $-0·4$ V; 2, $-0·2$ V; 3-5, $-0·4$ V; 6-8, $-0·6$ V; 9-13, $-0·8$ V (S.C.E.) 200 mV/cm.

REDUCTION IN RANGE I

In acid media two one-electron waves $(i_1)_1$ and $(i_1)_2$ are observed at potentials E_1^{I} and E_2^{I}, followed at potential E_1^{II}, by another one-electron wave (observed for ketones only). The properties of these waves can be explained by scheme (18)-(24), corresponding to a sequence (H^+, e, e, H^+, H^+, e):

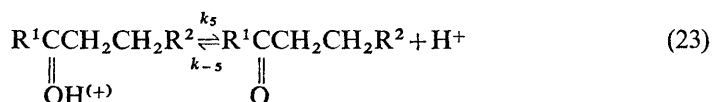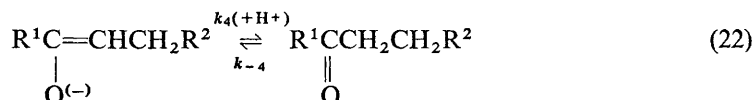$$\underbrace{R^1COCH{=}CHR^2}_{H^+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R^1COCH{=}CHR^2 + H^+ \qquad pK_1 \qquad (18)$$

$$\underbrace{R^1COCH{=}CHR^2}_{H^+} + e \underset{E_1^{\mathrm{I}}}{\rightleftharpoons} \underbrace{R^1\overset{\bullet}{C}OCH{=}CHR^2}_{H} \qquad (i_1)_1 \qquad (19)$$

$$\underbrace{R^1\overset{\bullet}{C}OCH{=}CHR^2}_{H} + Hg \overset{k_2}{\rightarrow} \text{organomercury compound} \qquad (20a)$$

$$2R^1COCH\overset{\centerdot}{\overbrace{=\!CHR^2}} \overset{k_3}{\longrightarrow} dimers \qquad\qquad (20b)$$
$$\underset{H}{\underbrace{}}$$

$$R^1COCH\overset{\centerdot}{\overbrace{=\!CHR^2}} + solvent \rightarrow product \qquad\qquad (20c)$$
$$\underset{H}{\underbrace{}}$$

$$R^1COCH\overset{\centerdot}{\overbrace{=\!CHR^2}} + e \underset{E_2^{\mathrm{I}}}{\rightarrow} R^1\underset{\underset{O^{(-)}}{|}}{C}\!=\!CHCH_2R^2 \qquad (i_{\mathrm{I}})_2 \quad (21)$$
$$\underset{H}{\underbrace{}}$$

$$R^1\underset{\underset{O^{(-)}}{|}}{C}\!=\!CHCH_2R^2 \overset{k_4(+H^+)}{\underset{k_{-4}}{\rightleftharpoons}} R^1\underset{\underset{O}{\|}}{C}CH_2CH_2R^2 \qquad\qquad (22)$$

$$R^1\underset{\underset{OH^{(+)}}{\|}}{C}CH_2CH_2R^2 \overset{k_5}{\underset{k_{-5}}{\rightleftharpoons}} R^1\underset{\underset{O}{\|}}{C}CH_2CH_2R^2 + H^+ \qquad\qquad (23)$$

$$R^1\underset{\underset{OH^{(+)}}{\|}}{C}CH_2CH_2R^2 + e \underset{E_1^{\mathrm{II}}}{\rightarrow} R^1\underset{\underset{OH}{|}}{\overset{\centerdot}{C}}CH_2CH_2R^2 \qquad (i_{\mathrm{II}})_1 \quad (24)$$
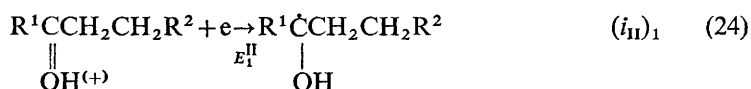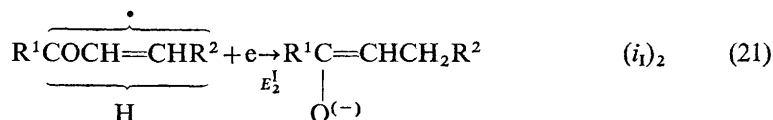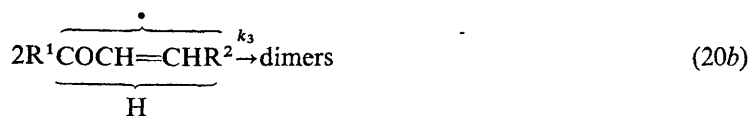
Apart from the number of electrons transferred which can be determined coulometrically, the shifts of half-wave potentials support the above scheme. The half-wave potential of waves $(i_{\mathrm{I}})_1$ and $(i_{\mathrm{II}})_1$ are shifted towards more negative potentials with increasing pH, that of wave $(i_{\mathrm{I}})_2$ remains pH independent. Atomic absorption spectroscopy and determination of mercury in the vapours indicates that the organomercury compound is formed at the limiting current of the first wave. It seems that process (20a) predominates at the dropping mercury electrode similarly as process (20a) was found to participate for methyl vinyl ketone[49] using a mercury pool electrode. The absence of either of the three most probable dimers (E)-(G) has been proved by the fact that the controlled potential electrolysis product does not give a wave corresponding to a R^1CO grouping (this excludes E and G), that it does not react either with periodic acid (excluding F) or with bromine (excluding F and G).
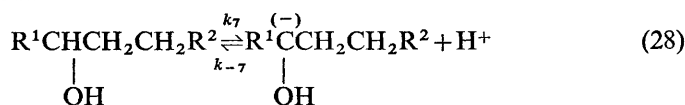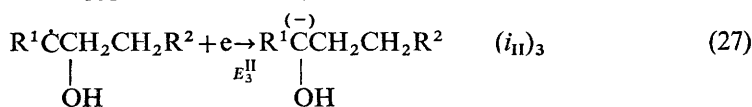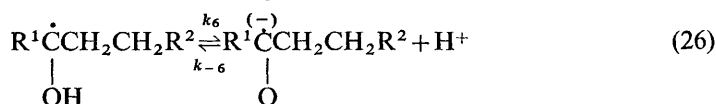
$$\begin{array}{ccc}
& \underset{\underset{O H}{|}}{O H} & \\
R^1COCH_2\underset{|}{C}H\!-\!R^2 & R^1\!-\!\underset{|}{C}CH\!=\!CHR^2 & R^1COCH_2\underset{|}{C}HR^2 \\
R^1COCH_2\underset{}{C}H\!-\!R^2 & R^1\!-\!\underset{|}{C}CH\!=\!CHR^2 & R^2CH\!=\!CH\underset{}{C}\!-\!R^1 \\
& OH & OH \\
(E) & (F) & (G)
\end{array}$$
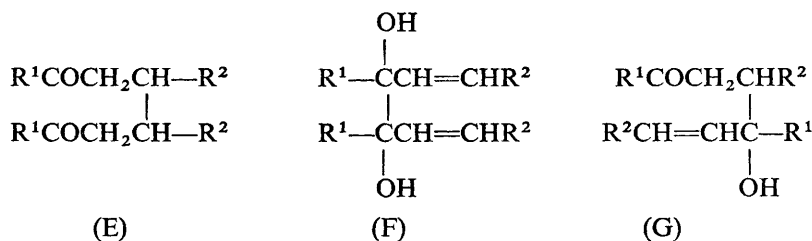
Radical $R^1\overset{\centerdot}{C}(OH)\,CH_2CH_2R^2$ formed in step (24) can undergo reactions (3)-(5). To achieve their maximum wave-heights corresponding to one-electron reductions the establishment of equilibria (18), (22) and (23) must be fast.
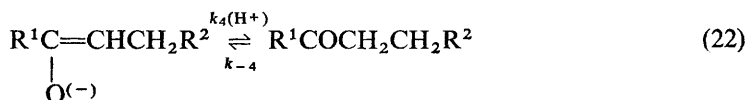
REDUCTION IN RANGE II

In the medium pH-range usually between pH 5 and 7 the two one-electron waves of unsaturated ketones $(i_I)_1$ and $(i_I)_2$ are followed by a two-electron wave $(i_{II})_3$. With some ketones, e.g, phenyl vinyl ketone, the first two waves coalesce in this region into one two-electron wave i_I. For unsaturated aldehydes the development of the wave $(i_{II})_3$ is prevented by hydration. The reduction follows the scheme (18)-(22) and (25)-(28), corresponding to the sequence (H⁺, e, e, H⁺, e, H⁺, e, H⁺) or (H⁺, e, e, H⁺, e, H⁺, H⁺, e) :

$$R^1COCH_2CH_2R^2 + e \xrightarrow[E_3^{II}]{} R^1\overset{(-)}{C}CH_2CH_2R^2 \qquad (i_{II})_3 \qquad (25)$$
$$\underset{O}{|}$$

$$R^1\overset{\bullet}{C}CH_2CH_2R^2 \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} R^1\overset{(-)}{C}CH_2CH_2R^2 + H^+ \qquad (26)$$
$$\underset{OH}{|} \qquad\qquad \underset{O}{|}$$

$$R^1\overset{\bullet}{C}CH_2CH_2R^2 + e \xrightarrow[E_3^{II}]{} R^1\overset{(-)}{C}CH_2CH_2R^2 \qquad (i_{II})_3 \qquad (27)$$
$$\underset{OH}{|} \qquad\qquad \underset{OH}{|}$$

$$R^1CHCH_2CH_2R^2 \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} R^1\overset{(-)}{C}CH_2CH_2R^2 + H^+ \qquad (28)$$
$$\underset{OH}{|} \qquad\qquad \underset{OH}{|}$$
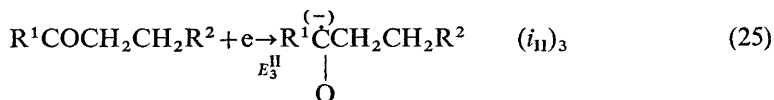
The half-wave potentials of wave $(i_I)_1$ or combined wave i_I are pH-dependent, those of wave $(i_I)_2$ and $(i_{II})_3$ are pH-independent. The potential of the step (27) is so close to or even more positive than, that of step (25) that only one two-electron step $(i_{II})_3$ is observed. To reach the full heights of the waves equilibria (18), (22) and (26) must be rapidly established.
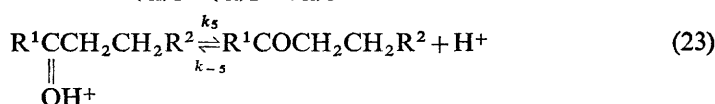
INTERMEDIATE RANGE BETWEEN I AND II

In this pH-range, usually between pH 3 and 6, the height of waves $(i_I)_1$ and $(i_I)_2$ remains unchanged, but that of wave $(i_{II})_1$ decreases in a shape of a dissociation curve. Simultaneously the total height of waves $(i_{II})_1 + (i_{II})_2 + (i_{II})_3$ changes, reaching a minimum in this pH-range and increasing both toward acid and alkaline pH-region.* The increase to lower pH-values corresponds to the acid-catalyzed enolate-ketone conversion (22), the increase toward higher pH-values to base catalyzed conversion (22). The reason for the changes in the wave i_{II} are hence due to the fact that equilibria (22) and (23) are no longer rapidly established :

$$R^1C{=}CHCH_2R^2 \underset{k_{-4}}{\overset{k_4(H^+)}{\rightleftharpoons}} R^1COCH_2CH_2R^2 \qquad (22)$$
$$\underset{O^{(-)}}{|}$$

governing total height

$$(i_{II})_1 + (i_{II})_2 + (i_{Ii})_3$$

$$R^1CCH_2CH_2R^2 \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} R^1COCH_2CH_2R^2 + H^+ \qquad (23)$$
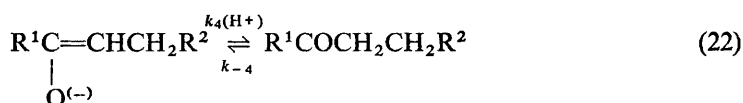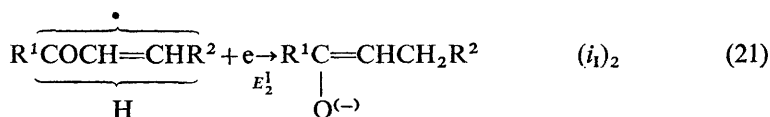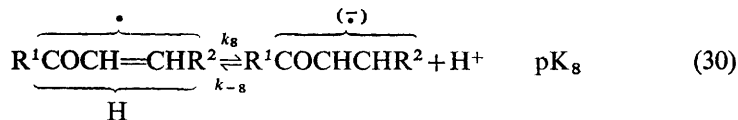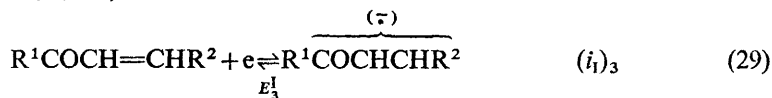$$\underset{OH^+}{\|}$$

governing relative height of $(i_{II})_1$

$$(i_{II})_1 : [(i_{II})_1 + (i_{II})_2 + (i_{II})_3]$$

* Wave $(i_{II})_2$ corresponding to the reduction of the radical $R^1\overset{\bullet}{C}OHCH_2CH_2R^2$ is usually overlapped by the current of the supporting electrolyte or by wave $(i_{II})_3$.
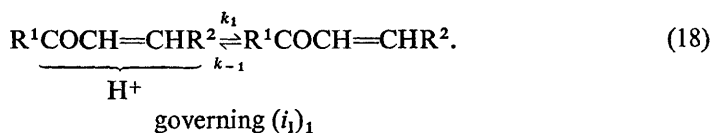
REDUCTION IN RANGE III

In this pH-range, which is usually narrow and occurs at about pH 8-9, the two-electron wave $(i_I)_3$ is followed by another two-electron wave $(i_{II})_3$. The reduction follows the scheme (29), (30), (21), (22), (25), to (28) and corresponds to the sequence (e, H⁺, e, H⁺, e, H⁺, e, H⁺):

$$R^1COCH{=}CHR^2 + e \rightleftharpoons \overbrace{R^1COCHCHR^2}^{(\div)} \qquad (i_I)_3 \qquad (29)$$
$$E_3^I$$

$$\overbrace{R^1COCH{=}CHR^2}^{\bullet} \underset{k_{-8}}{\overset{k_8}{\rightleftharpoons}} \overbrace{R^1COCHCHR^2}^{(\div)} + H^+ \qquad pK_8 \qquad (30)$$
$$\underbrace{\phantom{R^1COCH{=}CHR^2}}_{H}$$

$$\overbrace{R^1COCH{=}CHR^2}^{\bullet} + e \xrightarrow{E_2^I} R^1C{=}CHCH_2R^2 \qquad (i_I)_2 \qquad (21)$$
$$\underbrace{\phantom{R^1COCH{=}CHR^2}}_{H} \qquad\qquad\quad | \atop O^{(-)}$$

$$R^1C{=}CHCH_2R^2 \underset{k_{-4}}{\overset{k_4(H^+)}{\rightleftharpoons}} R^1COCH_2CH_2R^2 \qquad (22)$$
$$| \atop O^{(-)}$$

followed by the individual steps (25)-(28). To give the observed two-electron wave $(i_I)_3$ potentials E_3^I and E_2^I must be either similar or E_2^I more positive than E_3^I. In order to give a two-electron wave $(i_{II})_3$, the establishment of the equilibrium (22) must be fast. pH-independent half-wave potentials of both two-electron waves $(i_I)_3$ and $(i_{II})_3$ are in agreement with the above scheme. For aldehydes $R^1COCH_2CH_2R^2$ (where $R^1 = H$) the height of the wave $(i_{II})_3$ is governed by the rate of dehydration of the aldehyde group.
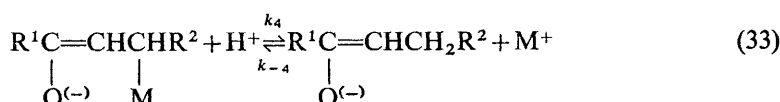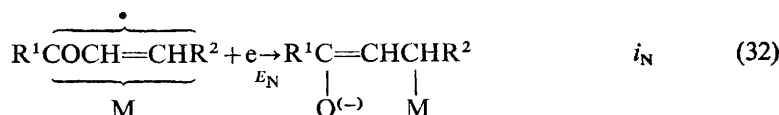
INTERMEDIATE RANGE BETWEEN II AND III

In this pH-range usually between pH 4 and 7, a decrease of wave $(i_I)_1$ can be observed in the form of a dissociation curve with a corresponding increase in the waves $(i_I)_2 + (i_I)_3$. The rate of reaction (18) governs the height of wave $(i_I)_1$:

$$R^1COCH{=}CHR^2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R^1COCH{=}CHR^2. \qquad (18)$$
$$\underbrace{\phantom{R^1COCH{=}CHR^2}}_{H^+}$$
$$\text{governing } (i_I)_1$$

Alternatively, when waves $(i_I)_1$ and $(i_I)_2$ previously merged into one single two-electron wave (i_I) (for which a shift of half-wave potentials was observed), the half-wave potential of the first combined two-electron wave becomes, with increasing pH, independent of pH for over more than one pH-unit. In the latter case waves (i_I) and $(i_I)_3$ are not separated, but their separation can be detected in some cases from logarithmic analysis. The value of pK_1' of reaction (18) is decisive for the pH at which the half-wave potential of wave (i_I) becomes pH-independent.

In the same pH-range, an increase in the concentration of neutral salts, in particular those with caesium or tetraalkylammonium cations, cause an increase of a new wave i_N in the potential range between $(i_I)_1$ and $(i_I)_2$ which grows at the expense of wave $(i_I)_2$. The plot of the height of wave i_N as a function of the logarithm of the metal concentration has a shape of a dissociation curve (fig. 10) the inflexion point of which

depends on the nature of the cation. This indicates that the cation of the added salt interacts with the radical formed in the first electron uptake. The species formed in this interaction is reduced in competition with the radical. One possible explanation is formulated in eqn. (31)-(33):
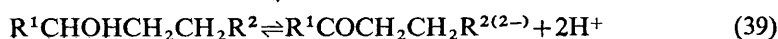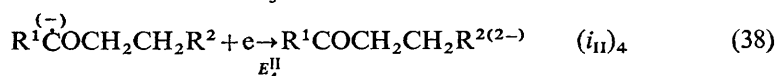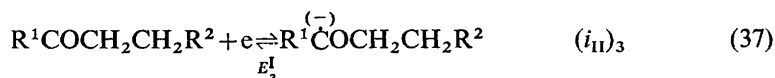
$$\overbrace{R^1COCH\!=\!CHR^2}^{\bullet}+M^+\underset{k_{-N}}{\overset{k_N}{\rightleftharpoons}}\overbrace{R^1COCH\!=\!CHR^2}^{\bullet}+H^+ \qquad K_N \qquad (31)$$
$$\underbrace{}_{H}\qquad\qquad\underbrace{}_{M}$$

$$\underbrace{\overset{\bullet}{R^1COCH\!=\!CHR^2}}_{M}+e\overset{E_N}{\rightarrow}R^1C\!=\!CHCHR^2 \qquad\qquad i_N \qquad (32)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\underset{O^{(-)}}{\big|}\ \underset{M}{\big|}$$

$$\underset{\underset{O^{(-)}}{\big|}\ \underset{M}{\big|}}{R^1C\!=\!CHCHR^2}+H^+\underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}}\underset{\underset{O^{(-)}}{\big|}}{R^1C\!=\!CHCH_2R^2}+M^+ \qquad\qquad (33)$$

To observe the wave i_N between $(i_I)_1$ and $(i_I)_2$ it is necessary that $|E_1| < |E_N| < |E_2|$. The height of the wave i_N is given by eqn. (34). Because the equilibrium constant of reaction (31) is not known, it is impossible to separate the effects of the nature of the cation on the equilibrium constant K_N of reaction (31) and on the rate constant (k_N).

$$\frac{i_N}{(i_I)_1+(i_I)_2+i_N}=1+\frac{0.886(k_N t_1/K_N)^{\frac{1}{2}}[M^+]}{1+0.886(k_N t_1/K_N)^{\frac{1}{2}}[M^+]}. \qquad (34)$$

REDUCTION IN RANGE IV

In this pH-range, usually above 11 or 12 when the solution contains only sodium or lithium cations and the ionic strength is 0·1 or less, two one-electron waves $(i_I)'_3$ and $(i_I)_4$ are observed, followed by the reduction wave of the saturated ketone or aldehyde i_{II}. This reduction of the species $R^1COCH_2CH_2R^2$ can also occur in two one-electron steps or in one two-electron step. In this pH-range it is important to compare the waves extrapolated to zero times (and possibly to record at lower temperatures) to prevent the homogeneous chemical reactions, such as addition of the hydroxyl group to the double bond and consecutive processes,[46] to complicate the polarographic curves. The reduction follows the scheme (29), (35)-(39) and corresponds to the sequence (e, e, H+, H+, e, e, H+, H+) or (e, e, H+, H+, e, H+, e, H+).

$$R^1COCH\!=\!CHR^2+e\underset{E^I_3}{\rightleftharpoons}\overbrace{R^1COCHCHR^2}^{(-)} \qquad (i_I)'_3 \qquad (29)$$

$$\overbrace{R^1COCHCHR^2}^{(-)}+e\underset{E^I_4}{\rightarrow}R^1COCHCHR^{2(2-)} \qquad (i_I)_4 \qquad (35)$$

$$R^1COCH_2CH_2R^2\rightleftharpoons R^1COCHCHR^{2(2-)}+2H^+ \qquad (36)$$

$$R^1COCH_2CH_2R^2+e\underset{E^I_3}{\rightleftharpoons}R^1\overset{(-)}{C}OCH_2CH_2R^2 \qquad (i_{II})_3 \qquad (37)$$

$$R^1\overset{(-)}{C}OCH_2CH_2R^2+e\underset{E^{II}_4}{\rightarrow}R^1COCH_2CH_2R^{2(2-)} \qquad (i_{II})_4 \qquad (38)$$

$$R^1CHOHCH_2CH_2R^2\rightleftharpoons R^1COCH_2CH_2R^{2(2-)}+2H^+ \qquad (39)$$

In agreement with this scheme are the half-wave potentials of wave $(i_l)'_3$ which is pH independent and of wave $(i_l)_4$ which is pH-independent below pK_8 corresponding to reaction (30) but shifted towards more negative values at pH $> pK_8$. The arguments for the formulation of eqn. (37)-(39) are the same as those used for the set of reactions (6), (12)-(14).
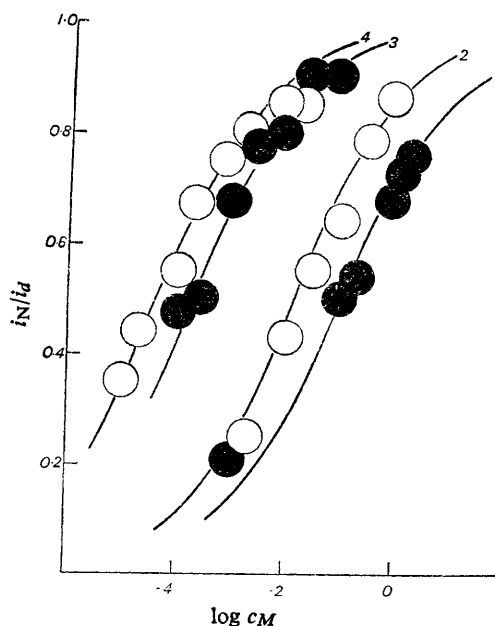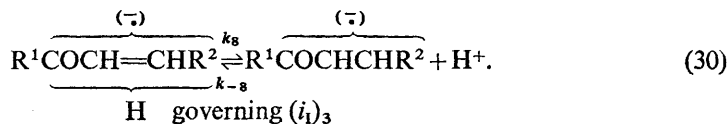

FIG. 10.—Dependence of i_N on cation concentration; recorded for 2×10^{-4} M cinnamaldehyde in a 2 % ethanolic acetate buffer pH 4·7, containing varying amounts of neutral salts. (1) Na$^+$; (2) Cs$^+$; (3) N(CH$_3$)$_4^+$; (4) N(C$_2$H$_5$)$_4^+$.

INTERMEDIATE RANGE BETWEEN III AND IV

In this pH-range, usually between pH 10 and 13, the decrease of wave $(i_l)_3$ from a two-electron process to a height corresponding to a one-electron step [denoted here as $(i_l)'_3$] takes place in the shape of a dissociation curve. The rate of reaction (30) with constant k_{-8} governs the height of the wave $(i_l)_3$:

$$\overbrace{R^1COCH}^{(\bar{\cdot})} = CHR^2 \underset{k_{-8}}{\overset{k_8}{\rightleftharpoons}} \overbrace{R^1COCHCHR^2}^{(\bar{\cdot})} + H^+. \qquad (30)$$
$$H \quad \text{governing } (i_l)_3$$

The change of the wave $(i_l)_3$ with pH follows eqn. (15), with the corresponding increase in wave $(i_l)_4$.

In this pH-range an increase of cation concentration, particularly of those with a larger ionic radius like caesium or tetra-alkyl ammonium results in an increase of a new wave (i_M) in the potential range between $(i_l)'_3$ and $(i_l)_4$ (fig. 11). The height of wave i_M increases with the logarithm of the metal ion concentration in the form of a dissociation curve (fig. 12), the position of which depends both on the nature of the cation and of the carbonyl compound involved. This indicates that monovalent cations can compete with protons for the radical ion. Even if the nature of the bond

of the metal ion in the species formed cannot be identified, it is possible to formulate the reaction giving rise to the wave i_M as follows:
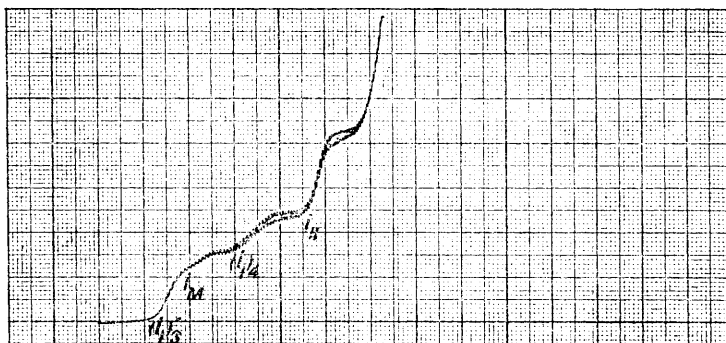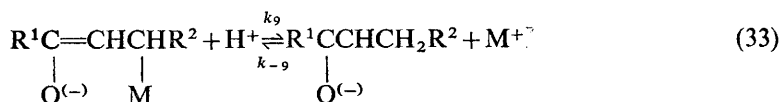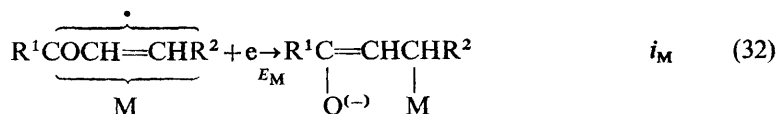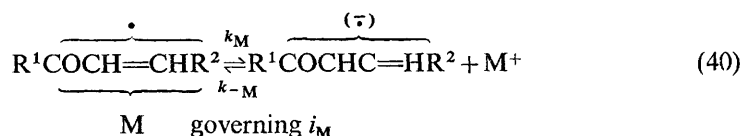
$$R^1COCH=CHR^2 \underset{k_{-M}}{\overset{k_M}{\rightleftharpoons}} R^1COCHC=HR^2 + M^+ \qquad (40)$$

$$M \qquad \text{governing } i_M$$

$$R^1COCH=CHR^2 + e \underset{E_M}{\rightarrow} R^1C=CHCHR^2 \qquad i_M \qquad (32)$$
$$\qquad\qquad\qquad\qquad\qquad\quad |\quad\quad |$$
$$M \qquad\qquad\qquad O^{(-)}\quad M$$

$$R^1C=CHCHR^2 + H^+ \underset{k_{-9}}{\overset{k_9}{\rightleftharpoons}} R^1CCHCH_2R^2 + M^{+\cdot} \qquad (33)$$
$$|\quad\quad |\qquad\qquad\qquad\qquad |$$
$$O^{(-)}\quad M \qquad\qquad\qquad O^{(-)}$$

FIG. 11.—Polarographic curve of cinnamaldehyde in 0·1 M lithium hydroxide. 2×10^{-4} M cinnamaldehyde recorded in a 2 % ethanolic solution containing 0·1 M lithium hydroxide and 0·4 M lithium chloride, curve starts at −0·8 V (S.C.E.).
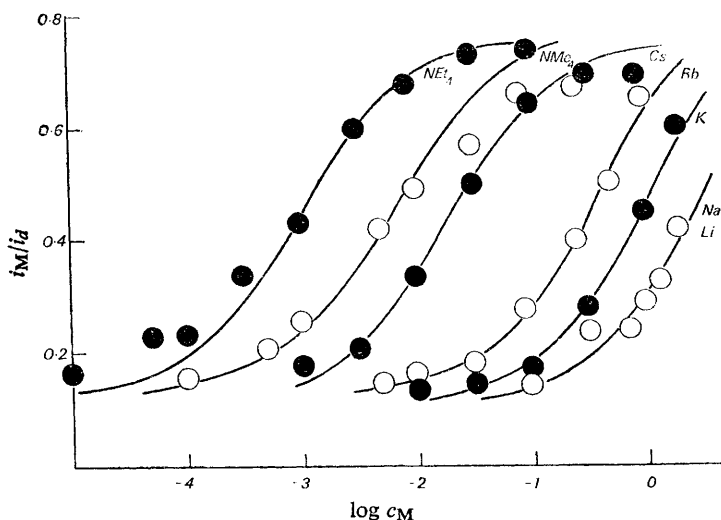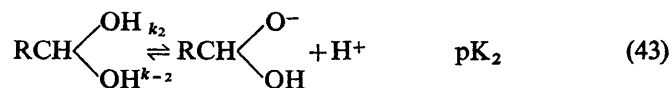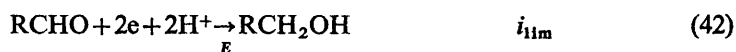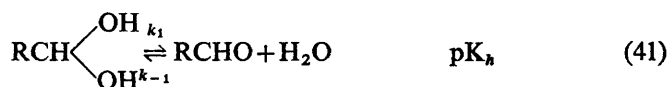

FIG. 12.—Dependence of i_M on cation concentration; recorded for 2×10^{-4} M cinnamaldehyde in a 2 % ethanolic 0·1 M lithium hydroxide solution containing varying amounts of neutral salts.

The value of E_M must fulfil condition $|E_3| < |E_M| < |E_4|$. The height of wave i_M can be calculated using eqn. (34).

ALIPHATIC ALDEHYDES

In the reduction of α,β-unsaturated aldehydes the wave i_{II}, consecutive to the first two-electron reduction of the double bond, was attributed to the reduction of the saturated aldehyde $R^2CH_2CH_2CHO$. Because, apart from formaldehyde,[50-52] our understanding of the polarographic reduction of saturated aldehydes is fragmentary, it was necessary to examine this problem. For this purpose the polarographic behaviour of the following aldehydes (RCHO) was examined: $R = H$, $CH(CH_3)_2$, $CH(C_2H_5)_2$, $CH_2C_6H_5$, CH_3, $CH(C_6H_5)CH_3$ and $CH_2CH_2C_6H_5$, but only the latter three in detail.

Polarographic waves of formaldehyde[50-52] increase with increasing pH, reach a maximum value at a pH about 13 and decrease at higher pH-values.* This behaviour was interpreted by the following set of eqn. (41)-(43):

$$\text{RCH}\begin{smallmatrix}\diagup OH \; {}_{k_1} \\ \rightleftharpoons \\ \diagdown OH^{k-1}\end{smallmatrix} \text{RCHO} + H_2O \qquad\qquad pK_h \qquad (41)$$

$$RCHO + 2e + 2H^+ \underset{E}{\rightarrow} RCH_2OH \qquad\qquad i_{lim} \qquad (42)$$

$$\text{RCH}\begin{smallmatrix}\diagup OH \; {}_{k_2} \\ \rightleftharpoons \\ \diagdown OH^{k-2}\end{smallmatrix} \text{RCH}\begin{smallmatrix}\diagup O^- \\ \\ \diagdown OH\end{smallmatrix} + H^+ \qquad pK_2 \qquad (43)$$

Only the aldehydic (dehydrated) form was considered to be electroactive. The increase at pH < 13 was attributed to the base catalysis of the dehydration reaction (41), the decrease at pH > 13 to the equilibrium (43). Originally[50] it was considered that it was the position of the equilibrium (43) which was shifted with increasing pH; later,[53] when the kinetic character of the current after this decrease had been proved, the diminishing rate of the protonation reaction (43) with a rate constant k_{-2} was considered. In all instances only the fully protonated form $RCH(OH)_2$ was considered to undergo dehydration.

The aldehydes studied differ from formaldehyde in four aspects: (a) whereas for formaldehyde only about 0·1 % is present in equilibrium as the free aldehydic form, for phenylacetaldehyde it is already 5 % and for all other compounds studied the free aldehydic form is present in 30-50 %; (b) whereas for formaldehyde the maximum wave-height corresponds only to some 15 % of the diffusion-controlled limiting current, for all of the aldehydes studies the current reached or almost reached the theoretical value for a two-electron diffusion-controlled process (with the exception of 3-ethyl-butyraldehyde (fig. 13). (c) The sensitivity towards catalysis by bases other than OH^- is smaller for the aldehydes studied than for formaldehyde. (d) Finally, the decrease of current above pH 13 observed for formaldehyde was observed only for some of the studied aldehydes, whereas with others the current after reaching the maximum value remained unchanged.

Whereas the first three differences are quantitative in nature and can reflect the changes in reactivity with structure, the last difference might indicate a qualitative

* Homogeneous chemical reactions indicated by changes in heights of aldehyde waves with time were also studied, but in this discussion, unless otherwise stated, the values of current described are those extrapolated to time zero.

difference in the individual steps involved in the electrode process and therefore was studied in detail. At 20°C the decrease was observed for phenylacetaldehyde and 2-phenylpropionaldehyde, but not for acetaldehyde and 3-phenylpropionaldehyde. The data obtained for isobutyraldehyde do not allow one to decide into which group it belongs (fig. 13). When the current for 2-phenylpropionaldehyde with increasing pH decreased below 50 % of the original height, it was possible to confirm its partly
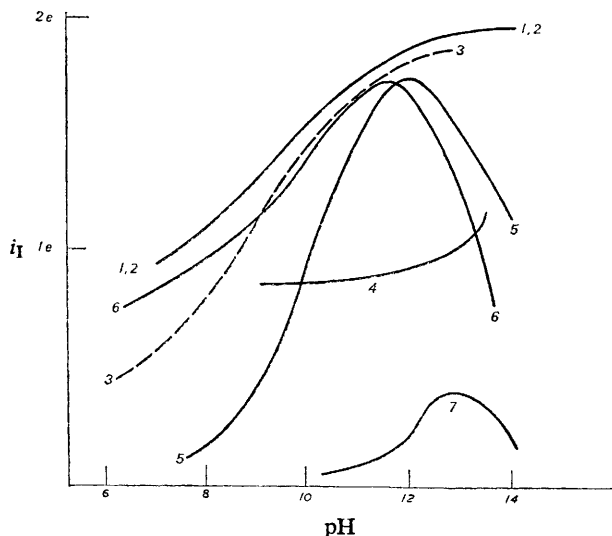

FIG. 13.—Dependence of the limiting currents of saturated aldehydes on pH. (1), (2), acetaldehyde, 3-phenylpropionaldehyde; (3), iso-butyraldehyde; (4), 2-ethylbutyraldehyde; (5), phenylacetaldehyde; (6), 2-phenylpropionaldehyde; (7), formaldehyde.

kinetic character. For aldehydes bearing a phenyl group of the α-carbon, formation of a moderately strong new peak in the u.-v. spectra at 280-300 mμ was observed in strongly alkaline media. The height of this peak increased with increasing pH in the shape of a dissociation curve (with pK $\approx$ 12·5 for 2-phenylpropionaldehyde). The band was observed in a wave-length range where carbanions of acetylacetone and ethyl acetoacetate give absorption bands of comparable molar extinction. The absorption band at 280-300 mμ therefore can be ascribed to the carbanion:
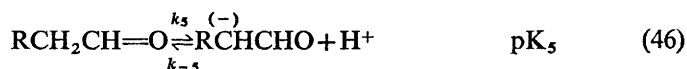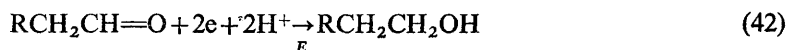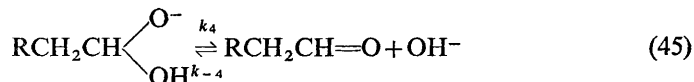
$$\overset{(-)}{RCHCH} \leftrightarrow RCH\!\!=\!\!CH$$

$$\underset{O}{\overset{\|}{}} \qquad \underset{O^{(-)}}{\overset{|}{}}$$
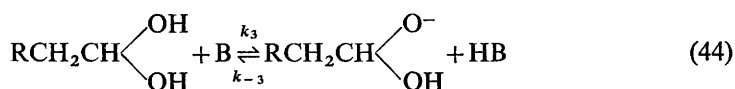
$$(H) \qquad (J)$$
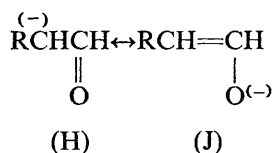
For phenylacetaldehyde and 2-phenylpropionaldehyde the band at 280-300 mμ reaches its maximum value practically immediately after mixing, so that if the attribution of this peak is correct, the formation of the carbanion is a relatively fast reaction.

On the other hand, for acetaldehyde and 3-phenylpropionaldehyde the half-time of formation of the peak at about 280 mμ is approximately 15 min. Hence the chemical reaction in homogeneous solution is in this case a relatively slow process, and the bands at 280 mμ correspond to products or intermediates of homogeneous chemical reactions.
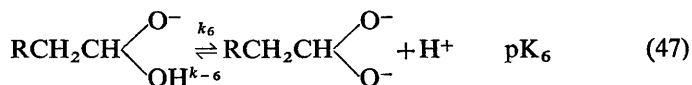
There are some arguments against formulation of the processes accompanying reduction of saturated aldehydes as (41)-(43). Observation [53] of a kinetic current in 5 M LiOH for formaldehyde would demand a considerably lower pK_2-value, than the value 13·27 reported [55] for formaldehyde for reaction (43). If the presence of reaction (43) were decisive for the decrease of current at pH > 13, it would be difficult to understand that for formaldehyde ($pK_2 = 13·27$) a marked decrease is observed, whereas for acetaldehyde ($pK_2 = 13·57$) there is no decrease. It is difficult to explain such substantial changes in k_{-2} with a small change in K_2. Moreover, the deviation of the specific rate constant for the reaction with hydroxyl ions from the Brönsted plot [54] indicates that either hydroxyl ions play a special role in this reaction or their mechanism differs from that obeyed by other bases. Such a role of hydroxyl ions does not follow from reactions (41)-(43). Finally, all currently proposed mechanisms for the base-catalyzed dehydration involve consideration of the monoanion $RCH(O^-)OH$ as an intermediate because the hydration can be formulated as a nucleophilic attack by hydroxyl ions. Hence an increase in the concentration of the monoanion with increasing pH would result in an increase and not a decrease in the dehydration rate. Moreover, when a species is considered to be an intermediate as the monoanion in eqn. (45) it cannot at the same time be considered to be a non-reactive " storage " as the same monoanion in eqn. (43).

In view of the above polarographic and spectroscopic evidence it seems probable that the scheme involved in the reduction of saturated aldehydes can be formulated as (44), (45), (42), (46) :

$$RCH_2CH{\Big\langle}{}^{OH}_{OH} + B \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} RCH_2CH{\Big\langle}{}^{O^-}_{OH} + HB \qquad (44)$$

$$RCH_2CH{\Big\langle}{}^{O^-}_{OH}{}^{k_{-4}} \underset{}{\overset{k_4}{\rightleftharpoons}} RCH_2CH{=}O + OH^- \qquad (45)$$

$$RCH_2CH{=}O + 2e + 2H^+ \underset{E}{\rightarrow} RCH_2CH_2OH \qquad (42)$$

$$RCH_2CH{=}O \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} \overset{(-)}{RCHCHO} + H^+ \qquad\qquad pK_5 \qquad (46)$$

The decrease in the wave-height with pH (at $t=0$) occurs for phenylacetaldehyde and 3-phenylpropionaldehyde, where the equilibrium (46) is not established too slowly. The observed current is then limited by the rate of protonation with rate constant k_{-5}. The spectroscopically-determined value for pK_5 for 2-phenylpropionaldehyde is $pK_5 \approx 12·5$ and in agreement with the theory the polarographic $pK' = 13·7$ (defined as the value of that pH at which the current decreases to 50 % of the diffusion governed value) is by more than one pH unit higher.

Another possibility, viz., the formation of dianion (47), cannot be excluded as an explanation for the decrease in current at pH > 13. Such dianions are postulated as intermediates, e.g., in Canizzaro reaction.[56] Nevertheless, it would be more difficult to bring this explanation into an agreement with the spectroscopic evidence.

$$RCH_2CH{\Big\langle}{}^{O^-}_{OH}{}^{k_{-6}} \underset{}{\overset{k_6}{\rightleftharpoons}} RCH_2CH{\Big\langle}{}^{O^-}_{O^-} + H^+ \qquad pK_6 \qquad (47)$$

EFFECTS OF STRUCTURE OF THE ALDEHYDE AND NATURE OF CATIONS

The half-wave potentials of aldehydes RCHO in 0·1 M lithium hydroxide containing 0·4 M lithium chloride show shifts with the change in structure of R that fit the Taft equation $\Delta E_{\frac{1}{2}} = \rho_\pi^* \sigma_x^*$ for $\rho_\pi^* = 0.2$ V. Hence the polar effect has a predominating influence on the reduction.

As the values of the hydration equilibrium constants K_h are unknown for most compounds studied, it was not possible to calculate values of the rate constants. Because in the reactions involved the reaction with hydroxyl ions predominates, it was possible to plot the values pK' (corresponding numerically to the pH at which the aldehyde wave reaches 50 % of the limiting diffusion current) against Taft polar substituent constants σ^*. It seems that the rate and equilibrium constants in reactions (44) and (45) are affected predominantly by the polar effects of the group R.

FIG. 14.—Effect of added cations on the half-wave potential of 5×10^{-4} M aldehyde recorded in a 5 % ethanolic borate buffer pH 9·3 containing 0·5 M neutral salt (added as the chloride). acetaldehyde (circles); 3-phenylpropionaldehyde (halved points)
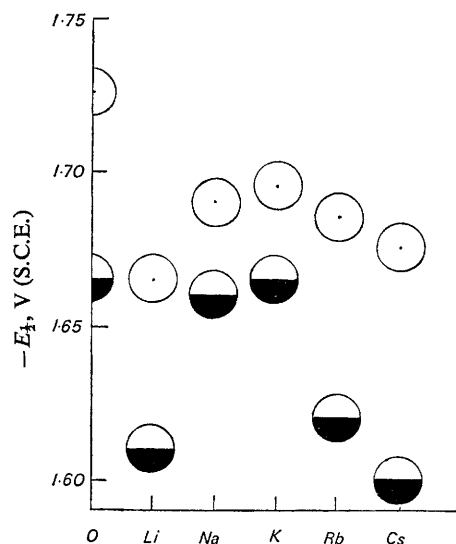
The influence of cations on the half-wave potentials (fig. 14) indicates that cations exert at least two effects and that these are in competition. Changes in the composition of the electrode double layer undoubtedly is one of the factors responsible for these phenomena.

CONCLUSIONS

The present study demonstrated the need for a selection of widely varied structures to get a deeper insight into the nature of the electrode processes, in particular, to distinguish the individual steps and their sequence. Some of the known facts have been interpreted, and some new observations explained. But simultaneously some new problems arise and they await solution which will only be achieved when sufficient breadth can be accompanied by sufficient depth of examination.

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