124. *The Depolarisation Potentials of Phenyl Alkyl Ketones in Acid, Neutral, and Basic Media at the Dropping-mercury Cathode.*

By W. Cule Davies and David P. Evans.

The depolarisation potentials of some phenyl alkyl ketones in acid, neutral, and basic media have been measured by the polarographic method of Heyrovský. The polarograms indicate that the depolarisation potentials are smaller (less negative) in solutions of low p_H than in neutral and alkaline solutions. As the length of the *n*-alkyl chain increases, the depolarisation potential of the ketone in a basic medium rises, and secondary alkyl groups have a larger effect in the same direction. In acid solution the depolarisation potentials vary irregularly. A study has been made of the heights of the waves given by acetophenone in solution in lithium hydroxide, and by both hydrion and acetophenone in solutions of constant hydrochloric acid concentration containing varying amounts of acetophenone.

The depolarisation potential * of acetophenone has been measured by several investigators using Heyrovský's polarographic method. Shikata and Tachi (*Mem. Coll. Agric. Kyoto*, 1930, **8**, 1) noted that it varied with the p_H of the medium, Winkel and Proske (*Ber.*, 1936, **69**, 693) measured it in N/10-ammonium and -lithium chloride, and Adkins and Cox (*J. Amer. Chem. Soc.*, 1938, **60**, 1151) also recorded a value with ammonium chloride as added

Table I.

Depolarisation Potentials of Acetophenone.

Expt. No.	M/20-COPhMe, c.c.	N/10-LiCl, c.c.	Cell potential, volts.	Anode potential, volts. obs.	Anode potential, volts. corr.	Corrected depolarisation potential, volts.
1	0·5	25	−1·65	0·008	0·344	−1·31
2	3·0	25	−1·66	0·012	0·348	−1·31
3	5·0	25	−1·66	0·011	0·347	−1·31
4	5·0	25	−1·67	0·012	0·348	−1·32
5	1·0	25 †	−1·67	0·030	0·366	−1·30
6	5·0	25 †	−1·71	0·040	0·376	−1·33
7	5·0 *	25	−1·67	0·011	0·347	−1·32
8	5·0 *	10 §	−1·70	−0·003	0·333	−1·37
		N/10-LiOH, c.c.				
9	2·0	25	−1·41	−0·246	0·090	−1·32
10	2·0	25	−1·42	−0·246	0·090	−1·33
11	5·0	25	−1·38	−0·260	0·076	−1·30
12	5·0	25 ‡	−1·42	−0·235	0·101	−1·32
13	5·0 *	25	−1·37	−0·273	0·063	−1·31
14	5·0 *	10 §	−1·42	−0·268	0·068	−1·35

Expt. No.	M/20-COPhMe, c.c.	N/10-LiCl, c.c.	N/10-HCl, c.c.	Cell potential, volts.	Anode potential, volts, obs.	Anode potential, volts, corr.	Corrected depolarisation potential, volts.
15	5·0	25	0·5	−1·18	0·010	0·346	−0·83
16	5·0	25	1·0	−1·15	0·008	0·344	−0·81
17	5·0	25	2·0	−1·15	0·008	0·344	−0·81
18	5·0	25	2·0	−1·15	0·005	0·341	−0·81
19	5·0	25	3·0	−1·14	0·004	0·340	−0·80
20	5·0	25	5·0	−1·14	0·000	0·336	−0·80
21	2·0	25	2·0	−1·18	0·035	0·371	−0·81
22	5·0 *	25	2·0	−1·15	0·003	0·339	−0·81
23	5·0 *	10 §	2·0	−1·17	−0·009	0·327	−0·84

* M/20-Acetophenone in 50% alcohol. † N/50-LiCl. ‡ N/50-LiOH.
§ With addition of 10 c.c. of alcohol.

---

* This refers to the potential of the mercury cathode at which the irreversible reduction of the depolariser takes place, and might be compared with the "apparent reduction potential" of Conant and Lutz (*J. Amer. Chem. Soc.*, 1923, **45**, 1047) for irreversible systems. It should not be confused with the potential as obtains in, *e.g.*, the reversible system benzoquinone–quinol (Conant and Fieser, *ibid.*, p. 2194).

electrolyte, but did not exactly specify the conditions. At the outset of the present work it was found that the depolarisation potential of acetophenone has the same value in lithium hydroxide as in lithium chloride solution, but in (hydrochloric) acid solution the value is appreciably lower. Several experiments have now been carried out to confirm and extend this observation (Table I). Whilst these were in progress, Adkins and Cox published an extensive table of depolarisation potentials of aldehydes and ketones in ammonium chloride and in tetramethylammonium hydroxide solution, which included values for *n*- and *iso*-butyrophenones. Their results showed that there were only small differences in the reduction potentials of these ketones. They did not attach significance to differences of less than 0·1 volt, but since our method affords depolarisation potentials reproducible to 0·01 volt and we have employed fully standardised conditions, it is considered that real significance can be accorded to much smaller differences than 0·1 volt in depolarisation potentials. Table II summarises our results.

TABLE II.

Depolarisation Potentials of Phenyl Alkyl Ketones.

Expt. No.	R in R·COPh.	Cell potential, volts.	Anode potential, volts,		Corrected depolarisation potential, volts.	Ground electrolyte.
			obs.	corr.		
1 *	Me	−1·67	0·011	0·347	−1·32	LiCl
2 *	Et	−1·67$_{5}$	0·009	0·345	−1·33	
3	Me	−1·70	−0·003	0·333	−1·37	
4	Et	−1·73	−0·008	0·328	−1·40	
5	Pr$^{\alpha}$	−1·74	−0·003	0·333	−1·41	
6	Pr$^{\beta}$	−1·77	−0·002	0·334	−1·44	
7	Bu$^{\alpha}$	−1·72	−0·003	0·333	−1·39	
8 *	Me	−1·37	−0·273	0·063	−1·31	LiOH
9 *	Et	−1·43	−0·244	0·092	−1·34	
10	Me	−1·42	−0·268	0·068	−1·35	
11	Et	−1·46	−0·246	0·090	−1·37	
12	Pr$^{\alpha}$	−1·46	−0·238	0·098	−1·36	
13	Pr$^{\beta}$	−1·51	−0·244	0·092	−1·42	
14	Bu$^{\alpha}$	−1·47	−0·244	0·092	−1·38	
15 *	Me	−1·15	0·003	0·339	−0·81	LiCl + HCl
16 *	Et	−1·21	0·004	0·340	−0·87	
17	Me	−1·17	−0·009	0·327	−0·84	
18	Et	−1·24	−0·012	0·324	−0·92	
19	Pr$^{\alpha}$	−1·18	−0·008	0·328	−0·85	
20	Pr$^{\beta}$	−1·22	−0·010	0·326	−0·89	
21	Bu$^{\alpha}$	−1·15	−0·010	0·326	−0·82	

Solutions.—The test solutions were made up from 5 c.c. of M/20-ketone solutions with additions as follows:

Expt. No.	Additions.
1 and 2	25 c.c. of N/10-LiCl.
3—7	10 c.c. of N/10-LiCl + 10 c.c. of EtOH.
8 and 9	25 c.c. of N/10-LiOH.
10—14	10 c.c. of N/10-LiOH + 10 c.c. of EtOH.
15 and 16	25 c.c. of N/10-LiCl + 2 c.c. of N/10-HCl.
17—21	10 c.c. of N/10-LiCl + 2 c.c. of N/10-HCl + 10 c.c. of EtOH.

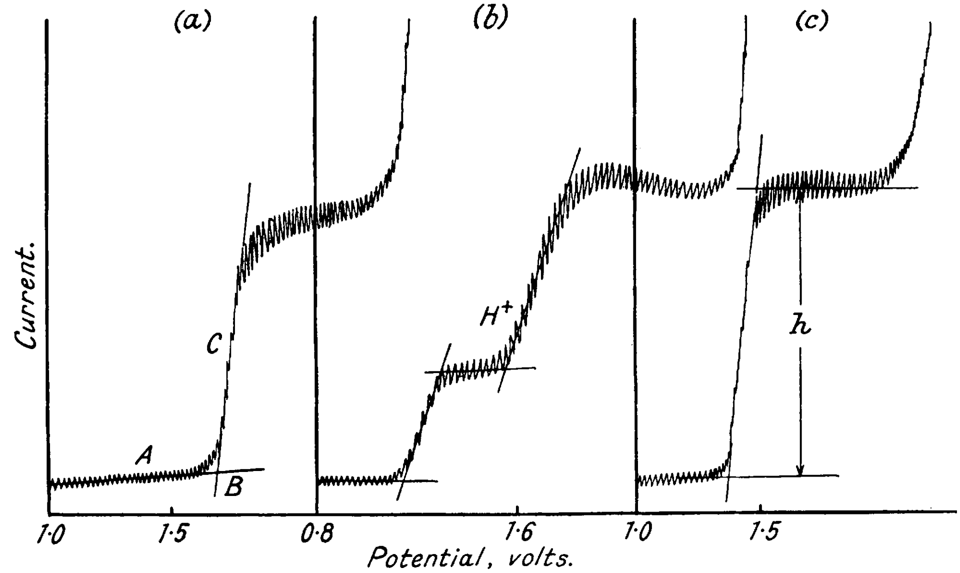
* The M/20-ketone solutions were made up in 50% alcohol–water; therefore, in these experiments the medium contained approximately 8% of alcohol, and in the others it consisted of 50% alcohol. Hydrogen was passed through the cell in every case for about 20 minutes in order to remove oxygen.

The electro-reductions of ketones are irreversible processes, so that doubt might be cast on the validity of comparing the numerical values of the depolarisation potentials of different ketones. The trend of the present results fits fairly well with what would be expected from structure, and the results of other polarographic investigations of large numbers of compounds in similar irreversible systems lead to the same conclusion (Semerano and Chisini, *Gazzetta*, 1933, **63**, 802; Winkel and Proske, *loc. cit.*; *Ber.*, 1936, **69**, 1917; *Angew. Chem.*, 1937, **50**, 18; Breyer, *Ber.*, 1938, **71**, 163; Adkins and Cox, *loc. cit.*; Shikata and Tachi, *Coll. Czech. Chem. Comm.*, 1938, **10**, 368). It seems to be a general rule, therefore, that the depolarisation potential of such substances varies with structure and substituents in a manner which can be predicted, at least qualitatively, from a knowledge of the electronic effects of such substituents.

EXPERIMENTAL.

The polarographic method consists essentially in applying a continuously increasing potential to a cell which has a pool of mercury as anode, mercury dropping from a capillary as cathode, and containing the substance being investigated, in this case the ketone, dissolved in a ground solution which contains an excess of an electrolyte (compare Glasstone, " The Electrochemistry of Solutions," London, 1930, p. 404). The current flowing through the cell is recorded in our instrument, made by Messrs. E. Leybolds Nachfolger A.-G., Köln–Bayenthal, on photographic paper. Polarograms of the type shown in Fig. 1 result.

FIG. 1.



(*Oxygen was removed in each case by passing hydrogen through the cell for* 20 *minutes.*)
(*a*) 5 *C.c. of* M/20-*acetophenone* (*in* 50% *alcohol*) *and* 25 *c.c. of* N/10-*lithium chloride. Galvanometer sensitivity,* 1/100.
(*b*) *Solution as in* (a), *but with addition of* 2 *c.c. of* N/10-*hydrochloric acid. Galvanometer sensitivity,* 1/200.
(*c*) 5 *C.c. of* M/20-*acetophenone* (*in* 50% *alcohol*) *and* 25 *c.c. of* N/10-*lithium hydroxide. Galvanometer sensitivity,* 1/75.

When the potential across the cell reaches the characteristic value associated with any reducible substance present, there is a rapid increase in the current, which finally reaches a more or less constant value (the saturation current). When the characteristic potential associated with another reducible substance is reached, a similar " step " or wave in the curve will result. The potential at which the " step " commences is variously known as the reduction, deposition, or depolarisation potential, and the height of the " step " is termed the wave height. The potential is defined in different ways by various authors. Shikata and Tachi use the method in which it is defined as the potential where the current increase reaches a definite value ($1{\cdot}9 \times 10^{-8}$ amp. per mv.). Heyrovský and Ilkovič (*Coll. Czech. Chem. Comm.*, 1935, **7**, 198) recommend the use of the half-wave potential; this method has the advantage that it gives a value which is independent of the concentration of the reducible substance, but it is not readily applicable always, especially in cases where the head of the wave has a shape as in Fig. 1(*a*). We have used Winkel and Proske's method, originally employed by Heyrovský. Reference to Fig. 1(*a*) will indicate the method adopted to determine the depolarisation potential. The potential between the anode and cathode corresponding with the point B (called hereafter the cell potential) where the lines AB and CB intersect is read off from the polarogram, and the anode potential is added; the resulting value is the depolarisation potential. Small changes in the concentration of acetophenone have little effect on the depolarisation potential as measured by this method (see Table I, Nos. 1, 2, and 3). The anode potential is measured against a calomel electrode, and consequently the depolarisation potentials are expressed with respect to the saturated, normal, or decinormal calomel electrode potentials as zero. This is a source of inconvenience in comparing the results of different workers, and it seems advisable to refer all depolarisation potentials to the normal hydrogen electrode potential, E^0_h, as arbitrary zero. This procedure has been adopted in the present work.

In Tables I and II, the heading " Cell potential " records the potential difference between the anode and the cathode of the cell of the polarograph at the point B on the polarogram, and under the heading " Anode potential, obs." the anode potentials are recorded referred to the N/10-calomel electrode potential as zero. The *E.M.F.* of the cell, anode–calomel electrode, was found by means of a valve electrometer potentiometer. The corrected anode potentials given in the next column were evaluated from the expression

$$\text{corrected anode potential} = 0{\cdot}336 + \text{observed anode potential}$$

and the corrected depolarisation potentials in the last column were calculated from the equation corrected depolarisation potential = observed cell potential at B + corrected anode potential. The values thus obtained are referred to the more general datum $E^0_h = 0$.

In Table I, col. 2 refers to the volume of an M/20-solution of acetophenone in 25% alcohol.

Relation between the Concentration of Acetophenone and Wave Height in Solutions of the Ketone in Lithium Hydroxide Solution.—When lithium hydroxide is employed as the ground electrolyte, the head of the wave due to acetophenone in the polarogram is almost horizontal, so the measurement of the wave height is rendered simpler than in, *e.g.*, lithium chloride solution where the head of the wave tends to curve upwards [compare Figs. 1(*a*) and 1(*c*)]. The wave height varies linearly with the concentration of acetophenone as shown below :

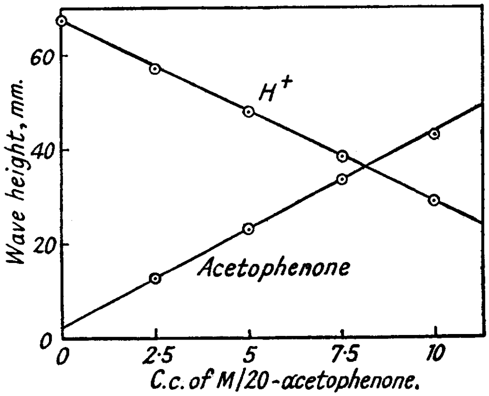


FIG. 2.

The wave heights are referred to a galvanometer sensitivity of 1/200. *Test solutions :* 10 *c.c. of* N/10-*lithium chloride,* 2 *c.c. of* N/10-*hydrochloric acid,* n *c.c. of* M/20-*acetophenone* (*in* 50% *alcohol*) *and alcohol to bring the total amount of alcohol equal to* 5 *c.c. in each case, diluted to* 25 *c.c. with water.*

[Ketone], g.-mols./l. × 10^3	2	4	6	8	10
Wave height, mm.	58	109	159	216	258
Wave height/[ketone]	29	27	27	27	26

In this table the wave heights are referred to a galvanometer sensitivity of 1/20. The test solutions were made by adding the requisite volume of M/20-acetophenone in 50% alcohol to 10 c.c. of N/10-lithium hydroxide, adding an amount of alcohol so that the total volume of alcohol (including that in the ketone solution) was 2·5 c.c., and finally diluting to 25 c.c. with water. An open beaker may be used as cell, since it is not necessary, in this case, to remove oxygen by passage of hydrogen or nitrogen. In the most dilute solution, however, where the greatest galvanometer sensitivity is employed, the measurement of the polarogram is facilitated by passing hydrogen and thereby eliminating the oxygen wave, which comes immediately before the acetophenone wave. Such a standardisation may be used for determining the concentration of acetophenone in an unknown solution, provided that the conditions of the experiment are kept the same. This refers especially to the capillary of the dropping-mercury cathode, the distances between the light source, galvanometer, and camera, and to some extent to the relative proportions of alcohol and lithium hydroxide.

The Reduction Potential of Hydrogen Ion and the Effect of the Addition of Acetophenone to an

Acid Medium.—A ground solution of 25 c.c. of N/10-lithium chloride to which portions of about 2—5 c.c. of N/10-hydrochloric acid had been added gave waves for hydrion from which the cell potential was found to be − 1·53 to − 1·54 volts (corrected potential = − 1·18 to − 1·19 volts). The addition of acetophenone hardly affected this cell potential. When acetophenone is added in successive portions to a ground solution of lithium chloride and a constant amount of hydrochloric acid, the wave height due to acetophenone is proportional to the concentration of ketone. On the other hand, the wave height due to hydrogen ion *decreases* linearly in such a way that *the sum of the wave heights due to acetophenone and hydrion in any solution is constant* (Fig. 2).

A ground solution of lithium chloride to which successive amounts of hydrochloric acid are added gives results which show that the wave heights vary linearly with the concentration of hydrogen ion (see Table III).

TABLE III.

$[H^+]$, g.-ions/l. × 10^3	4	8	12	16 *	20
Weight height, mm.	63	152	257	360	480
Wave height/($[H^+]$ − x)	25	23·4	24·3	24·8	25·9

(x = value of intercept on $[H^+]$ axis, *viz.*, 0·0015 g.-ion/l.)

The wave heights are referred to a galvanometer sensitivity of 1/100. Test solutions: 10 c.c. of N/10-lithium chloride, 2 c.c. of alcohol, and *n* c.c. of N/10-hydrochloric acid diluted to 25 c.c. with water.

In the polarograms from which the results in Table III were obtained there is a tendency for a current maximum (Hohn, "Chemische Analysen mit dem Polarographen," Berlin, 1937, p. 5) to occur before the normal saturation current is reached, especially in solutions containing larger amounts of hydrochloric acid. A well-defined current maximum appears in the hydrogen-ion wave when the experiment (marked * in Table III) using 4 c.c. of hydrochloric acid was repeated with the addition of a further 2 c.c. of alcohol.

The height, *h* [Fig. 1(*c*)], is a measure of the saturation current for the reaction concerned, and depends upon the rate of transfer of electrons from the cathode, and therefore upon the rate of reduction of the substance undergoing reaction. The greater the number of molecules in the vicinity of the cathode, the greater is the rate of reduction, and the current therefore increases with increasing concentration of reducible substance present in solution. Borcherdt, Meloche, and Adkins (*J. Amer. Chem. Soc.*, **1937**, **59**, **2171**) have shown that the wave height for a particular ketone is directly proportional to its concentration, an observation which is confirmed by our results for acetophenone in lithium hydroxide solution, and in lithium chloride solution containing hydrochloric acid. A linear relation also exists between the heights of the hydrogen-ion waves and the concentration of hydrion in solutions of hydrochloric acid containing lithium chloride as ground electrolyte.

The wave height due to hydrogen ion in solutions containing no ketone is a measure of the maximum rate (corresponding with the concentration) of reduction of hydrogen ion by the reaction

$$2H^+ + 2e = H_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (a)$$

which occurs at the cathode when the applied potential (corrected for the anode potential) reaches the reduction potential of hydrion (− 1·18 volt). This maximum rate varies with the hydrogen-ion concentration as shown in Table III. The fall in the wave height due to hydrogen ion on adding acetophenone to hydrochloric acid (Fig. 2) therefore indicates that the rate of reduction of hydrions by reaction (*a*) is steadily decreased. The reduction of acetophenone (which, of course, continues concurrently with that of hydrogen ion at the higher potentials) requires a definite amount of hydrogen ion for the reaction

$$COR_2 + 2H^+ + 2e = CHR_2{\cdot}OH \quad . \; . \; . \; . \; . \; . \; . \quad (b)$$

to proceed at the cathode. The remainder only is available for reduction to hydrogen. Moreover, since the *rate* at which hydrogen ion is used up in reaction (*b*) is equal to the *rate* of reduction of ketone, then, as the ketone concentration increases the amount of hydrogen ion available for reduction to hydrogen steadily decreases. Briefly we may write

$$L^a_h = K\{[H^+]_t - [\text{ketone}]\} = \text{constant} - K[\text{ketone}]$$

where L^a_h represents the wave height due to hydrogen ion, $[H^+]_t$ the total concentration of hydrogen ion, and K is a numerical constant. This expression shows that the plot of hydrion-wave heights against the concentration of ketone should be linear with a negative slope, as found in Fig. 2.

The ketones employed were prepared and purified by the methods described by Evans (J., 1936, 785) and Evans and Gordon (J., 1938, 1434).

DISCUSSION.

Our result for the depolarisation potential of acetophenone in lithium chloride solution (— 1·31 volts) agrees very well with that of Winkel and Proske (*loc. cit.*) which when referred to $E_h^0 = 0$ is — 1·32 volts. This affords strong evidence for the applicability of this method of evaluating the depolarisation potentials obtained by the polarographic method.

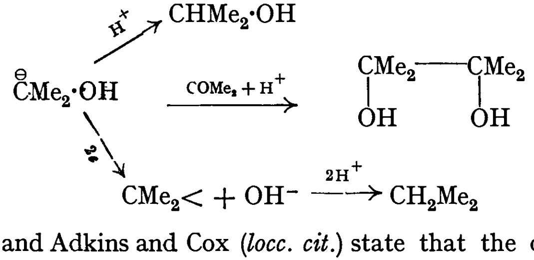
It will be seen from Table I that the depolarisation potential of acetophenone in neutral and in basic media is almost independent of the concentration of ketone, salt, alcohol, or hydrion within the limits studied. In experiments 8 and 14, however, the presence of approximately 50% alcohol increases the depolarisation potential slightly. The similarity of the depolarisation potentials in lithium chloride and hydroxide solution is possibly to be expected, since, if the reduction process is accompanied by liberation of hydroxyl ions, in lithium chloride solution the medium in the neighbourhood of the mercury drops will become alkaline (owing to the unbuffered character of the solution). As a result, however, of the constant renewal of the cathode surface and the agitation of the liquid by the falling drops, it is not expected that the alkalinity developed would be as great as in lithium hydroxide solution. Work is being continued on this aspect of the problem.

When the p_H is decreased considerably by addition of hydrochloric acid, the depolarisation potential falls from the mean value of — 1·31 to — 0·81 volt.* The fall is similar to that of the potential of the reversible hydrogen electrode with change of p_H from 10 to 1 and may be expressed by

$$D.P. = -0{\cdot}058\,p_H - k$$

where k is the difference in potential of the reversible hydrogen electrode and that of the mercury cathode at which reduction of ketone occurs, both electrodes being in the same solution.

A mechanism for the electrolytic reduction of acetone was recently put forward by Semerano (*Gazzetta*, 1932, **62**, 983; compare Müller, *Z. Elektrochem.*, 1927, **33**, 255) in which it was assumed that the initial stage consisted in the addition of water to give the dihydroxy-compound $CMe_2(OH)_2$, which, at the surface of the cathode, lost one hydroxyl group and gained two electrons to give the negative ion $\overset{\ominus}{C}Me_2{\cdot}OH$. The formation of the several products of reduction, *viz.*, *iso*propyl alcohol, pinacol, and propane was then represented by the following schemes :



Winkel and Proske and Adkins and Cox (*locc. cit.*) state that the depolarisation potential of acetone and aliphatic ketones cannot be measured with the polarograph since they do not give typical polarograms. The latter authors *suggest* that the depolarisation potential of acetone is approximately — 2·2 volts, which may account for the difficulty obtained in the polarographic measurement. Aliphatic aldehydes, however, give typical curves, and the same applies to acetophenone, benzaldehyde, and benzophenone. Moreover,

---

* After this paper was submitted, we noticed that of Winkel and Proske (*Ber.*, 1938, **71**, 1785), which records similar results for the influence of p_H on the depolarisation potentials of a number of ketones. The variation of the depolarisation potential with p_H is, however, not linear. It is suggested that the effective reducing agent is metal in alkaline solution and hydrogen in acid. Our views on the cause of the change in depolarisation potential with p_H are given in the text.

the depolarisation potentials fall in the order given in the following table, taken from the results of Winkel and Proske and Adkins and Cox.

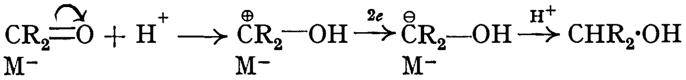
Depolarisation potentials (volts).

Compound.	Winkel and Proske. (In NH_4Cl.)	Adkins and Cox. (In NMe_4OH.)
Acetone	—	*ca.* −2·2
Acetaldehyde	−1·60	−1·87
Acetophenone	−1·44	−1·52
Benzaldehyde	−1·25	−1·34
Benzophenone	−1·23	−1·35
Chloroacetone	−1·13	—

It is evident that on replacement of R in CR_2O by an atom or group which is less electron repulsive (or more electron attractive) the depolarisation potential of the carbonyl compound is continuously decreased.

Practically identical wave heights for ketone are obtained in acid, neutral, or alkaline media containing the same concentration of ketone. This observation, coupled with Winkel and Proske's calculation, based on Faust's rule (*Ber.*, 1936, **69**, 705), indicates that in any of these solutions each molecule of ketone requires two hydrogen atoms for reduction, and that the principal product of reduction, therefore, is secondary alcohol. It might be noted that the Müller–Semerano reduction mechanism, in which the ketone hydrate is the substance reduced at the cathode, would only require one hydrogen atom to give the secondary alcohol. We, therefore, tentatively suggest the following alternative mechanisms for reduction, the second being more probable in alkaline solution.

(A) The primary process consists in the attraction of the ketone molecule towards the cathode, the positive end of the ketone dipole (*i.e.*, carbonyl carbon) being the attracted centre. This attraction initiates the electromeric change $>C\overset{\curvearrowright}{=}O \longrightarrow >\overset{\oplus}{C}{-}\overset{\ominus}{O}$, which is completed (whilst the ketone is attached to the cathode) by the addition of a hydrogen ion to carbonyl oxygen. The positively charged complex then takes on two electrons from the cathode to yield the negative ion $\overset{\ominus}{C}R_2\cdot OH$, which immediately combines with a hydrogen ion to yield the secondary alcohol :



$$\underset{M^-}{CR_2\overset{\curvearrowright}{=}O} + \overset{+}{H} \longrightarrow \underset{M^-}{\overset{\oplus}{C}R_2{-}OH} \xrightarrow{2e} \underset{M^-}{\overset{\ominus}{C}R_2{-}OH} \xrightarrow{H^+} CHR_2\cdot OH$$

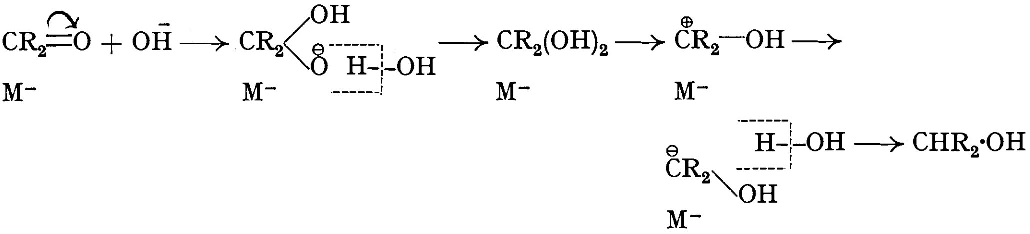
This scheme is very similar to that put forward by Burton and Ingold (J., 1929, 2022) for the reduction of olefinic compounds by sodium amalgam, *viz.*,

$$>C\overset{\curvearrowright}{=}C< + H^+ \longrightarrow >\overset{\oplus}{C}{-}CH< \xrightarrow{2e} >\overset{\ominus}{C}{-}CH< \xrightarrow{H^+} >CH{-}CH<$$

and the possibility of addition of hydrogen ion to carbonyl oxygen has been visualised by several authors.

The possibility of an equilibrium of the type $CR_2\overset{\curvearrowright}{=}O + \overset{+}{H} \rightleftharpoons \overset{\oplus}{C}R_2\cdot OH$ must not be overlooked, since the positive complex, if formed in solution, would readily be attracted to the cathode. The absence of any measurable amount of this positive complex was proved by the fact that the p_H of an N/100-hydrochloric acid solution in aqueous methyl alcohol (measured by means of a glass electrode) was the same as that of a similar solution containing 0·066 g.-mol./l. of acetophenone. This would indicate that, as mentioned above, in the electro-reduction the substance primarily attracted to the cathode is the ketone and not the positive complex.

(B) The primary process is again assumed to be the attraction of the ketone towards the cathode, with initiation of the change from carbonyl to semipolar form. If there is a plentiful supply of hydroxyl ions near the cathode, one of them may form a bond with the positive carbon to yield the negative complex ion $CR_2(OH)\cdot\overset{\ominus}{O}$. If this entity has sufficient energy, it may then extract a hydrogen ion from water to yield the dihydroxy-compound $CR_2(OH)_2$ (compare Semerano's mechanism):



Thus, two hydroxyl ions are given to the solution and two electrons are taken from the cathode. In (A) a similar state of electrical affairs exists, two hydrogen ions being taken from solution and two electrons from the cathode. Scheme (B) is similar to Semerano's except that (*a*) the primary process is assumed to be the attraction of ketone to the cathode with subsequent addition of hydroxyl ion, and (*b*) the necessity for dissociation of water molecules is made more apparent.

Some evidence in favour of these mechanisms is given below.

With regard to the depolarisation potentials of the phenyl alkyl ketones, CPhRO, the most interesting observations in the present work are (*a*) the gradual, but regular, trend towards higher depolarisation potentials in alkaline and neutral solution (containing 50% alcohol) as the length of the *n*-alkyl chain increases, (*b*) that under these conditions *iso*-butyrophenone has the highest depolarisation potential, and (*c*) that in the acid solutions there is some irregularity, the depolarisation potential of propiophenone being particularly high compared with the neighbouring phenyl *n*-alkyl ketones, that of *iso*butyrophenone slightly lower, whilst the depolarisation potentials of acetophenone, *n*-butyro- and *n*-valero-phenone are almost the same, that of the last being the smallest.

The value of the depolarisation potential of an acetophenone derivative is influenced by the polar effect of the substituent. For instance, the results of Winkel and Proske (*loc. cit.*) for the depolarisation potentials of acetophenone, *p*-methyl- and *p*-chloro-acetophenone in lithium chloride solution (referred to $E^0_h = 0$) are $-1{\cdot}32$, $-1{\cdot}38$, and $-1{\cdot}28$ volts, respectively. These, together with other results (see Adkins and Cox, *loc. cit.*), indicate that the electro-reduction of carbonyl compounds in slightly acid, neutral, or basic media is facilitated (*i.e.*, the potential is made smaller) by electron recession from the seat of reaction. We therefore conclude that as the *n*-alkyl chain, R in R·COPh, becomes longer the depolarisation potentials of the ketones in basic media should rise gradually owing to the increasing $+I$ effect of the alkyl group, which would resist both the approach of the ketone to the cathode and the addition of hydroxyl ion at carbonyl carbon. Secondary alkyl groups should have a larger effect upon the depolarisation potential than primary alkyl groups (compare the values of the activation energies for the base-catalysed prototropy of the same ketones; Evans and Gordon, *loc. cit.*). The results recorded in the first two sections of Table II are, therefore, to be anticipated. The similar trend in the activation energies, *E*, for the base-catalysed prototropy of these ketones (in aqueous acetic acid) and their depolarisation potentials (D.P.) in basic media is indicated in the following table.

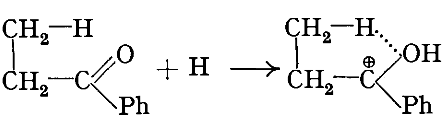
R in R·COPh	Me	Et	Pr^{α}	Pr^{β}	Bu^{α}
D.P., volts (basic medium)	$-1{\cdot}35$	$-1{\cdot}37$	$-1{\cdot}36$	$-1{\cdot}42$	$-1{\cdot}38$
E (base-catalysed prototropy), cals.	19,400	19,900	20,200	20,900	20,100

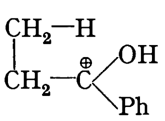
The changes in activation energies for the base-catalysed prototropy of these ketones were interpreted on the basis of the inductive effects of the alkyl substituents and the formation of an "activated complex" between the ketone and anion catalyst, and it seems likely that the changes in depolarisation potential in the series of phenyl alkyl ketones in basic media may be similarly explained.

There also exists a similarity in the trend of the depolarisation potentials of these ketones in acid solution and that of the activation energies for their acid-catalysed prototropy (Evans, J., 1936, 785).

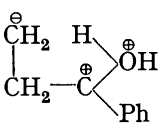
R in R·COPh	Me	Et	Pr^{α}	Pr^{β}	Bu^{α}
D.P., volts (acid medium)	−0·84	−0·92	−0·85	−0·89	−0·82
E (acid-catalysed prototropy), cals.	20,200	22,100	22,000	22,100	21,700

In both *E* and the depolarisation potential there is a large increase in passing from acetophenone to propiophenone, with a subsequent fall on proceeding to higher *n*-alkyl derivatives. The equality of the *E* values for propio- and *iso*butyro-phenone which indicates the operation of the Baker and Nathan effect (J., 1935, 1844; see Evans and Gordon, *loc. cit.*) is paralleled by the similarity of their depolarisation potentials in acid medium. The surprisingly large increase in *E* for the acid-catalysed prototropy on changing R from Me to Et was interpreted as being due to hydrogen-bond formation between β-methyl and carbonyl oxygen in the activated complex between ketone and catalyst, the inductive effect of the additional methyl group being too small (and in the wrong direction) to account for such a large increase in *E*. The similar trend of the depolarisation potentials appears to point to an analogous explanation for the high depolarisation potential of propiophenone; *i.e.*, during the approach of the hydrogen ion to the ketone [mechanism (A), p. 552] a hydrogen bond is formed as indicated by the dotted line shown below :





(I.)



(II.)

The product is a resonance hybrid of the forms (I) and (II). The formation of this hydrogen bond would decrease the electron density around the oxygen atom and cause an increase in the energy necessary for approach (or linking in reduction) of hydrogen ion.

The high depolarisation potentials of propiophenone and *iso*butyrophenone, compared with those of the other phenyl alkyl ketones in acid media, appear to point to a mechanism of reduction which includes the addition of hydrogen ion to the carbonyl oxygen as one step, and, therefore, form some evidence for mechanism (A).

It is unlikely that in basic catalysis the formation of a hydrogen bond would influence the energy of activation to any great extent (Evans and Gordon, *loc. cit.*; compare the results of Evans, Gordon, and Watson, J., 1937, 1425, on the hydrolysis of ethyl *o*-toluate). In this and similar base-catalysed reactions the anion catalyst is assumed to add to the carbonyl carbon, and, since the depolarisation potentials of the phenyl alkyl ketones in basic medium increase regularly as the alkyl series is ascended, it appears likely that addition of OH takes place during the electro-reduction of these ketones under the conditions studied.

Tatem Laboratories, University College, Cardiff.
The Technical College, Cardiff.

[*Received, October* 19*th*, 1938.]