# Mechanism of the Electrochemical Reduction of Phenyl Ketones

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Six ketones, studied polarographically and coulometrically, show the following behavior pattern: in acidic media all give one diffusion-controlled pH-dependent cathodic wave and a more negative pH-independent wave. The diffusion current constant increases with increasing pH to a maximum at pH 9 and then decreases, corresponding to a variation in the faradaic $n$ from 1 to 2 and then back to 1. The one pH-dependent wave observable above pH 6 approximates in height the sum of the waves indicated in the more acidic region. At higher pH, a third more negative wave appears. The only products isolable are pinacol (wave I in acidic media and above pH 9) and carbinol (waves II and III, and the combined wave between pH 6 and 9). Electrochemical reduction of ketones is best explained by a free radical mechanism: in acidic and neutral media the ketone diffuses into the electrode field and its carbonyl group is polarized; simultaneously, the carbonyl oxygen (now partially charged) attracts a proton, which process favors increased polarization; the protonated ketone completes its diffusion into the electrode interphase and acquires an electron, resulting in wave I; the free radical produced dimerizes to pinacol. Wave II results from 1-e reduction of the free radical to carbinol at more negative potential. Due to the pH-dependence of wave I, it and wave II merge into the combined wave. In alkaline media the mechanism is essentially the same, except that due to the relative proton scarcity, carbinolate free radical ion is formed along with the carbinol free radical; the more difficult reduction of the former accounts for the decreased magnitude of the combined wave and the appearance of wave III. The mechanism proposed is evaluated on the basis of the expected effects of structure. Previously proposed mechanisms are critically discussed.

Review of the literature on the polarography of aromatic ketones made apparent the need for a more accurately defined mechanism for ketone reduction at the dropping mercury electrode (D.-M.E.). Consequently, the polarographic behavior of five alkyl phenyl ketones (aceto-, propio-, n-butyro-, i-butyro- and pivalophenone) and of benzophenone was systematically investigated. Macroscale electroreductions were made to determine $n$ values (number of electrons transferred per molecule in the electrode process) and their variation with pH and to produce sufficient of the major reduction products at various pH levels to allow isolation and identification. From these studies and the literature data, a general mechanism for the electroreduction of ketones has been deduced and evaluated on the basis of expected structural effects.

## Electrochemical Behavior

**Summary of Previous Work.**—The many polarographic studies of alkyl phenyl ketones, which have been largely confined to investigation of acetophenone, have been critically summarized.[2] More recent studies[3] include a general equation,[3c] relating the structure of a carbonyl compound to its $E^0{}_{1/2}$ ($E_{1/2}$ at pH 0); this equation fails when extended to compounds and conditions not included in the original study. The equation makes no allowance for environmental factors known to influence polarographic data; its validity also has been questioned on theoretical grounds.[4]

The polarographic behavior of benzophenone, which has also been extensively studied, generally differs from that of the alkyl phenyl ketones in that a multiplicity of reduction waves in acidic media has

been observed by all investigators; few[3b,5] have observed more than one wave for the alkyl phenyl ketones, regardless of pH. The most useful benzophenone studies[6] indicate that it exhibits two waves in acidic media.

Controlled-potential macroscale electroreduction of benzophenone yielded benzpinacol as the only product at pH 1.3, and benzhydrol and a small amount of benzpinacol at pH 8.6; from this and the coulometric reduction of other carbonyl compounds. Pasternak[6a] concluded that in a ketonic or aldehydic carbonyl reduction at the D.M.E., the number of electrons involved can be validly estimated from the wave height, and the normal products are the dimer (a pinacol, unless the carbonyl group being reduced is conjugated with unsaturation, in which case the products become more complicated) and the secondary carbinol, the latter being predominant in alkaline solution. Gardner[6c] verified these results for acidic solution. Swann, et al.,[7] found the characteristic primary reduction product of the macroscale electroreduction of acetophenone at a mercury cathode to be the corresponding pinacol. The findings of Pasternak,[6a] Gardner[6c] and Swann[7] are in general agreement with those of the present investigators.

**Polarographic Behavior.**[8]—The ketones investigated give at least one well-defined, diffusion-controlled cathodic wave over the usual pH range (Table I, Fig. 1). Benzophenone gives two waves below pH 6; iso-butyrophenone exhibits two in pH 5.7 acetate buffer. Except for these pH-independent second waves, $E_{1/2}$ for all ketones becomes more negative with increase in pH. Decrease in temperature and increase in alcohol concentration shift $E_{1/2}$ to slightly more negative

(1) Eastman Kodak Company, Rochester, N. Y.

(2) I. M. Kolthoff and J. J. Lingane, "Polarography," 2nd Ed., Interscience Publishers, New York, N. Y., 1952; J. T. Leone, Ph.D. Thesis, University of Michigan, 1956.

(3) Generally, only the most pertinent or typical references are being cited. (a) C. Calzolari and C. Furlani, Ann. triest. cura univ. Trieste, Sez., [2], 21, 47 (1951); Boll. sci. fac. chim. ind., 12, 42 (1954); (b) I. A. Korshunov, A. S. Kirillova and Z. B. Kuznetsova, Zhur. Fiz. Khim., 24, 551 (1950): I. A. Korshunov, Z. B. Kuznetsova, L. N. Sazanova and A. S. Kirillova, Zavodskaya Lab., 16, 144 (1950): (c) D. M. Coulson and W. R. Crowell, THIS JOURNAL, 74, 1290, 1294 (1952).

(4) A. Pacault and R. Pointeau, Compt. rend., 236, 2060 (1953).

(5) S. Wawzonek and H. A. Laitinen, THIS JOURNAL, 63, 2341 (1941).

(6) (a) R. A. Pasternak, Helv. Chim. Acta, 31, 753 (1948); (b) M. Ashworth, Collection Czechoslov. Chem. Communs., 13, 229 (1948); (c) H. J. Gardner, Chemistry and Industry, 819 (1951); (d) R. A. Day, Jr., and J. J. Kirkland, THIS JOURNAL, 72, 2766 (1950); (e) R. A. Day, Jr., S. R. Milliken and W. D. Shults, ibid., 74, 2741 (1952).

(7) S. Swann, Jr., P. E. Ambrose, R. C. Dale, R. C. Rowe, H. M. Ward, H. D. Kerfman and S. Axelrod. Trans. Electrochem. Soc., 85, 231 (1944).

(8) Detailed data are available from the authors. Typical data are given in the figures and tables included in this paper.

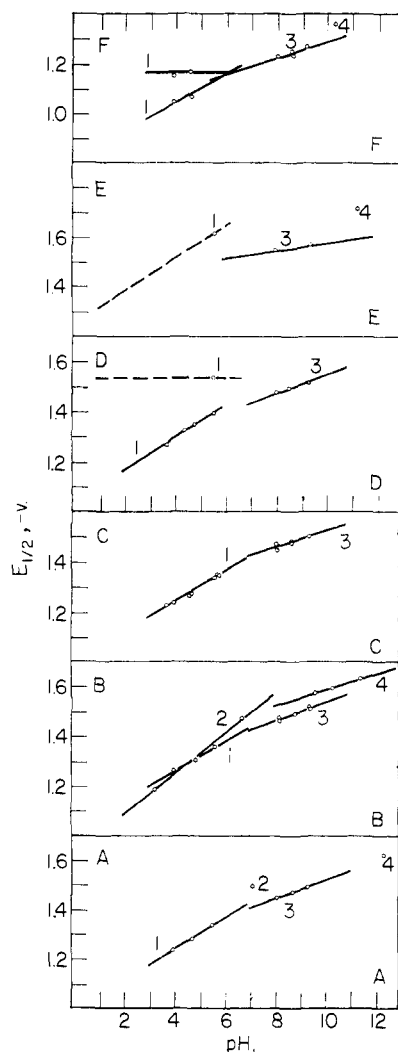Fig. 1.—Variation of $E_{1/2}$ with $p$H: A, acetophenone; B, propiophenone; C, $n$-butyrophenone; D, isobutyrophenone; E, pivalophenone; and F, benzophenone. Numbers refer to the buffer systems listed in Table IV.

values; effects of ionic strength and concentration are within experimental error.

The interrelated $I$ (diffusion current constant) and Ilkovic $n$ (for wave I when two appear) vary in a bell-shaped manner with $p$H (Fig. 2) and exhibit a much higher maximum for the $n$-alkyl phenyl ketones and benzophenone than for the branched alkyl ketones. Wave II (benzophenone and isobutyrophenone) is always, by comparison, approximately, a 1-e wave. Independent evaluation of $n$ from the Ilkovic equation is not absolutely valid since diffusion coefficients cannot be properly calculated; the Stokes–Einstein diffusion equation cannot be legitimately applied, since the molecules do not meet the specifications of being spherical[9a] and having a molecular weight in excess of 180.[9b] Diffusion coefficients were estimated from that of $o$-hydroxybenzyl alcohol (0.72 $\times$ $10^{-5}$ cm.$^2$/sec. in water)[10] by equating the ratio of the cube roots of

(9) (a) A. Einstein. Z. *Elektrochem.*, **14**, 235 (1908); (b) L. Friedman and P. G. Carpenter, THIS JOURNAL, **61**, 1745 (1939).

(10) E. W. Washburn, ed.. "International Critical Tables." Vol. V. McGraw–Hill Book Co., Inc., New York, N. Y., 1929, p. 71
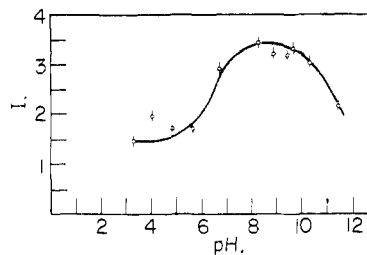


Fig. 2.—Variation of diffusion current constant, $I$ = $i_d/Cm^{2/3}t^{1/6}$, with $p$H for propiophenone.

the molecular volumes to the ratio of the respective diffusion coefficients; the value obtained for acetophenone is 0.70 $\times$ $10^{-5}$. Subsequent calculations showed $n$ for acetophenone to increase from 0.9 at $p$H 4 to 2.3 at $p$H 9 and then to decrease to 1.3 at $p$H 12.

TABLE I

VARIATION OF $E_{1/2}$ OF THE PHENYL KETONES WITH $p$H AT $25°$[a]

| Compound | Buffer no. | $E^{0}_{1/2}$, $-$v. | $B$, v./$p$H |
|---|---|---|---|
| Propiophenone | 2 | 0.904 | 0.083 |
| | 1 | 1.022 | .056 |
| | 3 | 1.153 | .038 |
| | 4 | 1.216 | .036 |
| Acetophenone | 1 | 0.990 | .060 |
| | 3 | 1.137 | .037 |
| $n$-Butyrophenone | 1 | 1.006 | .055 |
| | 3 | 1.146 | .036 |
| Isobutyrophenone | 1 | 1.031 | 1.063 |
| | 3 | 1.174 | 0.036 |
| Pivalophenone | 3 | 1.416 | .015 |
| Benzophenone | 1 | 0.819[b] | .054[b] |
| | 3 | 0.945[c] | .033[c] |

[a] $E_{1/2}$ values are presented in terms of the linear equation, $E_{1/2} = E^{0}_{1/2} - B(p$H$)$, where $E^{0}_{1/2}$ is the intercept, $E_{1/2}$ at $p$H 0, and $B$ is the slope or change in $E_{1/2}$ per $p$H unit. Since the latter varies with buffer system, the equation was used to correlate only data obtained within a given buffer system. [b] First of the two waves appearing in the acidic region; calculation of $E^{0}_{1/2}$ from Coulson and Crowell's[3o] generalized equation gave $-0.639$. [c] The combined wave appearing in the alkaline region.

Temperature coefficients of $i_1$ and variations with drop-time (mercury height) are those of a diffusion-controlled process. Except at higher concentrations in acetate buffer, $i_d$ is proportional to ketone concentration.

$\alpha$-Values, calculated from the slope of the polarographic wave ($\alpha$ = $0.056/(E_{1/4} - E_{3/4})$ at $25°$), are considerably smaller in the acidic and high alkaline regions than in the low alkaline region.

**Coulometric Behavior.**—Coulometry over the $p$H range of 3 to 12.5 showed conclusively that $n$ varies in a bell-shaped manner (Fig. 3). At a given $p$H $n$ decreases as follows[11]: at $p$H 4.8, $C_2$ (1.05) > $C_3$ (0.82), $C_4$ (0.82) > $i$-$C_4$ (0.67); at $p$H 8.6, $C_2$ (1.81) > $C_3$ (1.62), $C_4$ (1.61) > $i$-$C_4$ (1.51) > $t$-$C_4$ (1.26); and at $p$H 12.3, $C_2$ (1.12) > $C_4$ (0.86), $C_3$ (0.85) > $i$-$C_4$ (0.72) and $t$-$C_4$ (0.71). No data could be obtained for pivalophenone at $p$H 4.8 since its reduction coincided with the buffer discharge.

(11) To conserve space in comparing the ketones, the following abbreviations will be used: $C_2$, aceto-; $C_3$, propio-; $C_4$, $n$-butyro-; $i$-$C_4$, $i$-butyro-; $t$-$C_4$, pivalophenone; and Ph, benzophenone.

In view of the importance of the coulometric data, an evaluation of the properties of such data is justified, in particular as applied to the present study.

Coulometric $n$-values are not necessarily proportional to the polarographic diffusion currents, since diffusion does not enter into the calculation of coulometric $n$ values; they should, however, be approximately proportional to $I$ (diffusion current constant), provided no serious side reactions are involved. The present data show this to be generally true. If the current-producing polarographic process is kinetic-controlled, there may be considerable discrepancy between the coulometric and polarographic $n$ values.

The deviation of the coulometric $n$ values at $p$H 8.6 from the value of 2.0 expected for reduction to the carbinol can probably be ascribed to the formation of some pinacol, as well as to some possible side reactions invoking free radicals at the electrode. In comparing coulometric and polarographic data, one must keep in mind that there is more opportunity for free radical side reactions to occur during coulometry than at the DME, because of the greater free radical concentration present about the macro electrode. A small amount of benzpinacol, for example, has been identified in the reduction of benzophenone at $p$H 8.6.[6a]

The values for acetophenone at $p$H 4.8 and 12.3 similarly indicate the formation of some carbinol along with the pinacol, probably due to the difficulty of precise manual control of the potential. The latter, however, is not serious except in the acidic region where the first and second waves are very close together; in the case of acetophenone, the limiting current portion of wave I was much steeper than for the other ketones. These difficulties could be obviated if an automatic constant-potential electrolysis apparatus were used since then the precise $E_{1/2}$ potential could be maintained till reduction was complete. The procedure actually used involved running a slightly more negative potential on the limiting current portion of the curve when possible.

The presence of coulometric $n$-values less than 1.0 at $p$H 4.8 for the ketones other than acetophenone might be ascribed to the fact that, in the case of ketones other than acetophenone, it was noted that some resinous by-product was formed during the coulometric reduction. This by-product formed agglomerates which likely occluded and/or absorbed some of the unreduced ketone and thereby did not permit the reductions to go to completion. In addition, formation of the resin may have involved unreduced ketone. When macroscale electroreductions were run on acetophenone and propiophenone, the resinous by-product appeared in both cases. Attempts to identify the material were not successful. It is apparently a polymer which probably arises from free radical side reactions, e.g., from free radical addition across the carbonyl bond in unreduced ketone. Bromine addition and permanganate oxidation tests indicated that the resinous material contained some unsaturation. The mother liquor from the crys-
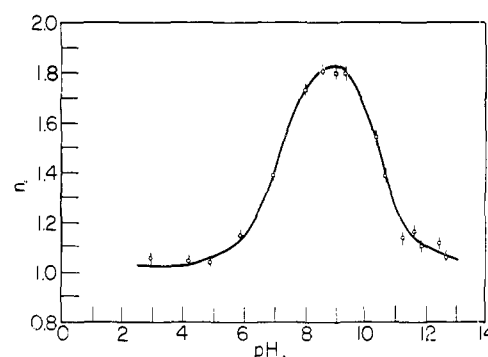


Fig. 3.—Variation with $p$H of $n$ (determined coulometrically) for acetophenone.

tallization of the pinacol also gave positive bromine and permanganate tests.

Positive identification of the resinous materials and determination of the exact mechanism of their formation were considered to be extraneous to the main purpose of the present investigation in being of little value for the clarification of the over-all ketone reduction mechanism. However, the existence of the resin does tend to corroborate the free radical mechanism. Swain, et al.,[7] also noted this resin but did not identify it.

**Macroscale Electrolysis.**—Reduction of propiophenone at $p$H 4.8 gave propiophenone pinacol; accidental features, e.g., color of the pinacol-containing fraction after distillation, crystallization of the oil on standing and its facile purification by a petroleum ether wash, were as described.[12] Reduction of acetophenone at $p$H 4.8 gave acetophenone pinacol.

The major product resulting from acetophenone at ca. $p$H 8 was not isolated, because the present coulometric data and those of Pasternak[6a] indicate that it is primarily carbinol; Pasternak did isolate benzhydrol from a macroscale electroreduction of benzophenone at ca. $p$H 8. Since the coulometric $n$ values decrease above $p$H ca. 9, it was considered necessary to isolate the major reduction product produced at higher $p$H. Reduction of acetophenone at $p$H 12.3 (phosphate buffer) and $E_{max}$ of $-1.6$ v. gave a product with the acetophenone pinacol melting point; a mixed melting point of the products obtained at $p$H 4.8 and 12.3 gave the same result.

### Ketone Reduction Pattern

**Number of Ketone Reduction Waves.**—The mechanisms generally advanced[6b,13] to explain the polarographic behavior of the alkyl phenyl ketones have many shortcomings. Conflicting reports concerning the number of waves exhibited by alkyl phenyl ketones below $p$H 6 has been a major obstacle in arriving at a generally acceptable mechanism. In the present study one well-defined wave usually was found. However, a small plateau, generally observed in the hydrogen discharge region of low $p$H acetate and MacIlvaine buffers, is assumed to be the beginning of a second wave.

(12) H. Sterns. Monatsh. Chem.. **26**, 1559 (1905).

(13) W. C. Davies and D. P. Evans. J. Chem. Soc., 546 (1939).

The latter assumption was examined by investigating $p$-bromoacetophenone (Table II). Both waves now shift to less negative potentials; in particular, wave II plateau shifts out of the buffer discharge region. This $E_{1/2}$ shift is due primarily to the $+I_s$, i.e., inductive effect, of the halogen substituent. Above 4.8 the *pH-dependent* first wave ($E_{1/2}$ becomes more negative with increasing $pH$) merges with the *pH-independent* second wave to give a "combined" wave. Neither wave is due to reduction of a carbon-halogen bond, since the latter is a 2-e process,[14] whereas the waves found are both approximately 1-e waves. These results emphasize the fact that, depending on environmental conditions, one or two waves can be observed in ketonic reduction in buffered acidic media; however, under most conditions wave II is distorted or masked by buffer discharge. Since fully aromatic ketones are reduced at lower potentials than mixed ones, it is not unusual to observe both waves for the former in the $pH$ range of 2 to 5 or 6.

Above $pH$ 6, only the combined wave is usually observed. As $pH$ is increased, its $i_d$ increases to a maximum (ca. $pH$ 9) and then decreases. Above $pH$ 9 a new wave appears at a more negative potential, whose height equals the decrease in height of the main wave.[5,6b]

**Reduction Path.**—Coulometric and polarographic data on the ketones exhibit a striking feature, indicating modification of the electrode process

TABLE II

EFFECT OF $pH$ ON $E_{1/2}$ AND $i_d$ OF $p$-BROMOACETOPHENONE[a]

| Buffer no. | $pH$ | Ketone concn., m$M$ | $E_{1/2}$, $-v.$ | $i_d$. $\mu a.$ |
|---|---|---|---|---|
| 2[b] | 3.2 | 0.200 | I 1.090 | 0.62 |
| | | | II 1.279 | .69 |
| 1[b,c] | 4.1 | .200 | I 1.164 | .45 |
| | | | II 1.277 | .44 |
| 1 | 4.8 | .200 | 1.240 | .95 |

[a] Measurements made at 25° at a corrected height of 58.3 cm., using capillary C. [b] Two waves appeared. [c] For waves I and II, $n$ equals 1.00 and 0.98, respectively. These values were approximated by comparing $i_d/C$ of each wave with that of acetophenone and relating the result to $n$ calculated for acetophenone.

with $pH$: the sharp rise of $n$ from 1 to a maximum of about 2, followed by an equally sharp decrease. There are two possible reduction paths for explaining this variation of $n$ as well as the variations in number and in size of the waves with $pH$: either (a) the 1-e process is the reduction of ketone to the free radical carbinol, which may dimerize to pinacol or be further reduced to carbinol, and the 2-e one is the reduction to carbinol through the free radical state; or (b) the 1-e process is the bimolecular reduction of ketone to pinacol and the 2-e one the direct reduction of ketone to carbinol.

Macroscale electroreduction at low and high $pH$ yields the pinacol as the major product; Pasternak[6a] isolated carbinol at about $pH$ 8. If mechanism (b) is assumed, a shift back to the bimolecular reaction or the free radical process has to be assumed to explain pinacol formation at high $pH$. In addition, if a bimolecular reaction is assumed, the dimerization is, by definition, essential for elec-

(14) P. J. Elving, *Rec. Chem. Progr.*, **14**, 99 (1953).

tron transfer and must take place simultaneously as a concerted process. Such a mechanism is not able to reconcile ketonic reductions, since it negates the possibility of a second wave at low $pH$ and contradicts the observed $pH$-dependence of the reduction of ketone to carbinol.

A second wave due to the direct, 2-e reduction of ketone to carbinol would present a paradox, since an energetically favorable process would be completely replaced by a less favorable one, i.e., more energy is needed to effect the direct reduction of ketone to carbinol ($E_{1/2}$ is more negative) than is needed to reduce ketone to pinacol. Further, it is highly improbable that both the bimolecular reduction to pinacol and the unimolecular reduction to carbinol occur simultaneously and independently; this is evident from the coulometric reduction product at the $E_{1/2}$ of wave II in acidic media[6a] being almost entirely carbinol, whereas from energy considerations ($E_{1/2}$ relationships) more pinacol would be formed if the processes were competitive (wave II would be much smaller than wave I).

Of the two waves observed at low $pH$ for $p$-bromoacetophenone, benzophenone and isobutyrophenone, which merge at about $pH$ 6 to form a $pH$-dependent wave, the $pH$-dependent wave I is due to reduction of ketone to pinacol and can be explained by either mechanism; the $pH$-independent wave II, however, involves reduction of carbinol free radical to carbinol. Therefore, the $pH$-independent, one-step, 2-e reduction of ketone to carbinol, the only answer possible if mechanism (b) is assumed, is contrary to observed behavior, i.e., the reduction of ketone to carbinol (combined wave) is $pH$-dependent.

## Electrochemical Reduction Mechanism

The free radical mechanism proposed essentially postulates (a) formation of a free radical as the fundamental process, (b) modification of this process with change in $pH$, i.e., formation of the corresponding free radical carbinolate ion in the alkaline region and (c) possible reduction to the carbinol of the resultant free radical and its ion before dimerization occurs.

**Acidic Region.**—The behavior of wave I is best explained as follows (Fig. 4): (a) as the ketone diffuses into the field of the electrode, the latter initiates polarization of the carbonyl group; (b) simultaneously, the carbonyl oxygen is attracted by neighboring protons, thus favoring increased polarization (the possibility that some of the ketone may be protonated before diffusing into the field of the electrode can be overlooked in the general mechanism since the effect of ionic strength is negligible, indicating that little, if any, of the diffusing material possesses a charge before it comes within the field of the electrode); and (c) the ketone, under the influence of both the protons and the field completes the diffusion (now supplemented by electromigration) into the interphase and acquires an electron.[15] The steps outlined are continuous and involve a transition state or species

(15) Since all ketones reducible at the D.M.E. are reduced at potentials beyond the electrocapillary maximum (mercury is charged negative), it is easy for the polarized or positively charged material to approach the electrode and even be adsorbed, if that be necessary.
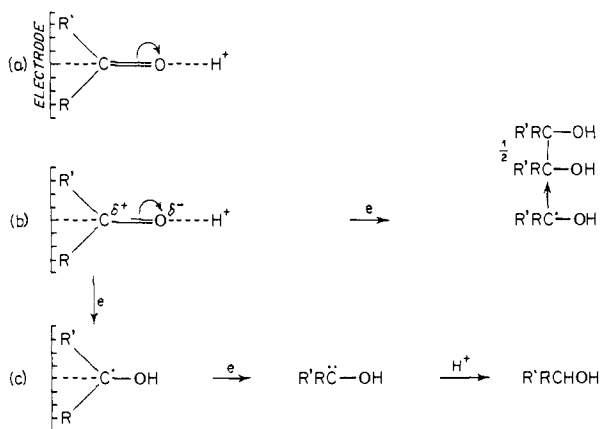
Fig. 4.—Reduction of a ketone at the D.M.E. in acidic and slightly alkaline media: (a) represents the initial diffu-sion-polarization process, (b) the formation of the carbinol-free radical (wave I), and (c) reduction of the carbinol-free radical (wave II) and subsequent acquisition of a proton. In neutral and slightly alkaline media the combined se-quence of (b) and (c) represents the combined wave.

in which as an electron is transferred to the car-bonyl carbon, a proton is simultaneously bonded to the carbonyl oxygen. The role of hydrogen ion in the "potential-determining" step and consequently in the transition state or species is made apparent by the strong $pH$-dependence of the reduction process (Fig. 1).

The free radical produced dimerizes to the pina-col until a potential is reached at which it is reduc-ible; it can then either dimerize to pinacol or be re-duced to carbinol; the latter process, which occurs almost exclusively, depending on structure [cf. subsequent discussion in Inductive and Steric Effects], is $pH$-independent and produces a second wave, found between $pH$ 3 and 6. As $pH$ increases, the shift of the $pH$-dependent wave I results in its eventual merger with the pH-independent wave II, with only the combined wave being usually ob-served above $pH$ 6.

**Alkaline Region.**—Several factors differentiate ketone behavior in alkaline media from that in acidic solution: the $pH$-dependence of the com-bined wave is much less than that of wave I in acidic media (Fig. 1); the combined wave height reaches a maximum at about $pH$ 9 and subse-quently decreases as the $pH$ increases (Fig. 2); a new, more negative wave (wave III) is observed above $pH$ 9.[5,6b] The mechanism outlined in the previous section satisfactorily accounts for these facts with only slight modification of the funda-mental process of the generation of a free radical (Fig. 5).

The observed $pH$-dependency, even though less-ened, indicates continued participation of protons in the "potential-determining" step of the reduction process. However, the decreased hydrogen ion concentration greatly diminishes the probability of forming an O—H bond simultaneously with electron transfer. Consequently, increasing amounts of car-binolate free radical ion are formed. The latter is not reduced at its formation potential and so dimerizes until its reduction potential is reached. The need

of additional energy for electroreduction of the anionic free radical arises from the coulombic re-pulsion between the electrode and the anion; further, the electron affecting the reduction now has to enter an area of increased electron density. The equilibrium shown in Fig. 5 is a possible source
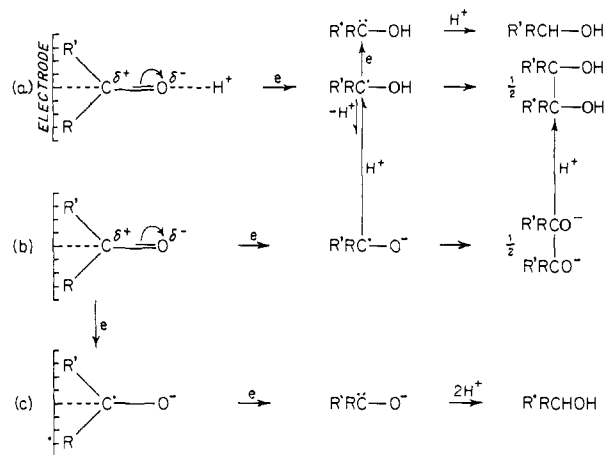


Fig. 5.—Reduction of a ketone at the D.M.E. in alkaline media above $pH$ 9: (a) and (b) represent processes which produce the combined wave, and (c) the process (reduction of carbinolate-free radical ion) causing wave III; the steps shown should be considered as continuous. The position of the equilibrium between carbinol-free radical (a) and its anion (b) is dependent on $pH$.

of carbinol free radical; if the carbinolate free radical ion (b) is at the electrode when the proton is acquired, the resultant carbinol free radical will be reduced to carbinol and thereby contribute to the magnitude of the combined wave. Conversely, if the anionic free radical has diffused away from the electrode, the carbinol free radical subsequently formed will not be reduced but will dimerize to pinacol.

Formation of the anionic free radical causes a decrease in magnitude of the combined wave above $pH$ 9, while its reduction results in the appearance of wave III. Since reduction of the carbinol free radical is unaffected by $pH$, the combined wave height increases to a maximum at about $pH$ 9 even though free radical formation becomes more diffi-cult with increasing $pH$. This is evident from the $E_{1/2}$–$pH$ relationship of the two waves (acidic re-gion) which merge to form the combined wave (Fig. 1F) and also accounts for its apparent re-versibility, i.e., the combined wave becomes steep, thus giving rise to high $\alpha$ values.

### Effect of Structure on $E_{1/2}$

Structural effects are generally excellent criteria for evaluating a mechanism with respect to its gen-erality and/or veracity. Change in molecular structure has marked effect on carbonyl group re-ducibility. Substitution of phenyl for methyl or hydrogen in acetaldehyde shifts $E_{1/2}$ to much less negative potentials. In acetophenone, replace-ment of methyl by $n$-alkyl has little effect on $E_{1/2}$; replacement by $t$-butyl or isopropyl makes $E_{1/2}$ more negative. The shifts of $E_{1/2}$ in carbonyl group reduction can be explained by electronic ef-

fects and to some extent by structural considerations; the mechanism proposed is in agreement with the observed structural effects.

**Inductive Effect.**—The role of the inductive effect, $+I_s$, in ketonic reduction becomes readily apparent on considering the decreasing ease of reduction in alkaline media for the three simple carbonyl compounds: $H.CO.H^{16a} > CH_3.CO.H^{16b} > CH_3.CO.CH_3.^{16c}$ This order is identical with the variation of the $+I_s$ of the substituent groups. Analogously, benzaldehyde is reduced more readily than acetophenone. Since the phenyl group has a very strong $+I_s^{17}$ (much stronger than hydrogen or methyl), benzaldehyde and acetophenone will be reduced more easily than their parent compound (AcH): $E_{1/2}$ vs. N.C.E.: $PhCOH^{6a}$ ($pH$ 11.3) $-1.48$ v., $PhCOMe^6$ $^a$($pH$ 11.3) $-1.64$ v. and $AcH^{16b}$ ($pH$ 10) $-1.80$ v.

On the basis of $+I_s$ for the groups attached to the carbonyl group, the expected order of ease of reducibility for the compounds covered in the present study is $Ph \gg C_2 > C_3$ and $C_4 > i\text{-}C_4 > t\text{-}C_4$. The observed order at $pH$ 9 is $Ph \gg C_2 > C_4 > C_3 > i\text{-}C_4 > t\text{-}C_4$; at $pH$ 5, $Ph \gg C_4 > C_2 > C_3 > i\text{-}C_4$ (no pivalophenone wave was observed). Only $n$-butyrophenone is out of line in being more easily reduced than expected. This deviation may be due to a tendency to hydrogen bond formation (three hydrogens on the $\gamma$-carbon are available for bonding with the carbonyl oxygen) which would aid in polarization of the carbonyl group. Electroreduction has been facilitated, where possibility of forming a six-membered ring exists.[18] The effect of such a hydrogen bond is more pronounced in acidic solution, probably because there is no stabilizing influence due to hyperconjugation.

It should be noted that addition of the second electron, i.e., reduction of the free radical, is facilitated the lower the electron density about the carbonyl carbon (the stronger the total $+I_s$). This reduced electron density would then cause an increase in the ratio of carbinol to pinacol formed in the region of the combined wave; actually, $n$ does vary in the order predicted in this region, i.e., $C_2 > C_3 > C_4 > i\text{-}C_4 > t\text{-}C_4$, and consequently the ratio of carbinol to pinacol would vary in the same manner.

**Correlation of $E_{1/2}$ with Polar Substituent Sigma Values.**—Correlation of $E_{1/2}$ values with polar substituent $\sigma$-values[19] would further support $+I_s$ as the cause for change in $E_{1/2}$ with structure. Except for 2 points out of 11, the ketones do correlate well in both acidic and alkaline media (Table III, Fig. 6); the deviations are approximately 0.035 v. with $n$-butyrophenone exhibiting a positive deviation in acidic solution, i.e., $E_{1/2}$ is less negative than expected, and acetophenone a negative deviation in alkaline media. The experimental error in measurement of $E_{1/2}$ is between 0.01 and 0.02 v.:

(16) (a) R. Bieber and G. Trumpler, *Helv. Chim. Acta*, **30**, 1109 (1947); (b) **30**, 2000 (1947); (c) M. B. Nieman and Z. V. Markina, *Zavodskaya Lab.*, **13**, 1177 (1947).

(17) H. Gilman, ed., "Organic Chemistry," Vol. II, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 1844.

(18) (a) J. E. Page, J. W. Smith and J. G. Waller, *J. Phys. Colloid Chem.*, **53**, 545 (1949); (b) J. Pearson, *Trans. Faraday Soc.*, **44**, 692 (1948).

(19) R. W. Taft, Jr., THIS JOURNAL, **75**, 4231 (1953).

$E_{1/2}$ is given to three decimal places in the tables for comparative purposes.

As previously mentioned, the hydrogen bond possible in $n$-butyrophenone would facilitate reduction by aiding in polarization of the carbonyl group. Conversely, in acetophenone possible hyperconjugation, i.e., ionization of a hydrogen alpha to unsaturation, would increase

TABLE III

CORRELATION OF $E_{1/2}$ OF THE PHENYL KETONES WITH POLAR SUBSTITUENT $\sigma$-VALUES$^a$

| | $-E_{1/2}$, v. | | |
| Compound | $pH$ 5 | $pH$ 9 | $\sigma^*$ |
| --- | --- | --- | --- |
| Benzophenone | $1.078^b$ | $1.223^b$ | 0.600 |
| Acetophenone | 1.289 | 1.477 | .000 |
| Propiophenone | 1.305 | 1.486 | − .100 |
| $n$-Butyrophenone | 1.285 | 1.481 | − .115 |
| $i$-Butyrophenone | 1.343 | 1.495 | − .200 |
| Pivalophenone | (No wave) | 1.550 | − .320 |

$^a$ The value of $\sigma^*$ is for the group R in R–Y, where Y is the functional group. In this case Y = $C_6H_5CO$–. $^b$ Since the benzophenone data were obtained on test solutions containing 19% ethanol, whereas all other data were obtained on solutions containing 9.5% ethanol, a correction was made for the effect of the additional alcohol based on shift in $E_{1/2}$ of $n$-butyrophenone observed when the alcohol concentration was increased from 9.5 to 19%. Consequently, $E_{1/2}$ values of benzophenone were made more positive by 0.44 and 1.77%, respectively, in acidic and alkaline media.

the electron density about the carbonyl carbon and thus exert a stabilizing influence. For the ketones studied, hyperconjugation would be expected to be operative only in alkaline media, while hydrogen bonding, though possible in both acidic and alkaline media, will exert the strongest effect in acidic media since there would be no stabilizing influence due to hyperconjugation.

**Steric Effects.**—Evaluation of steric effects in correlating shifts of $E_{1/2}$ with structure presents some difficulty, since there is no way to determine how to weigh the effects. Consequently, several steric factors will be considered as operating alone in reference to their possible effect on reducibility.

At the time of reduction the carbonyl group is assumed to be perpendicular to a plane tangent to the electrode surface with the carbonyl oxygen farthest from the electrode, as expected from coulombic effects. Using Fisher–Hirschfelder–Taylor models of the reacting molecules, the nearest possible approach to the electrode was determined by assuming several orientations for the substituents on the carbonyl carbon, placing the molecular model on a smooth surface and measuring the distance from the surface (which represents the electrode) to the carbonyl carbon. The following steric factors were thus evaluated: (a) nearest possible approach to the electrode, assuming no distortion of bond angles by the electrode field; (b) shielding of both the carbonyl carbon from back-side attack by electrons and the carbonyl oxygen from front-side proton attack; (c) relatively free rotation about the C–C bonds of the carbonyl group; and (d) hydrogen bonding.

The relative ease of reduction indicated by factor (a) is $C_2 > C_3 > C_4 > i\text{-}C_4 > t\text{-}C_4 > Ph$, i.e., since acetophenone can on the average achieve the closest approach to the electrode, the transfer of

electrons to its carbonyl carbon should be more facile than in the other ketones. Factor (b) indicates for the ease of reducibility: $C_2 > C_3 > C_4 >$ Ph $> i\text{-}C_4 > t\text{-}C_4$, i.e., acetophenone offers the least shielding to electrons and protons, and pivalophenone the most. Factor (c), which represents the ease with which the molecule orients itself to the position of most facile reduction, gives the following order of reducibility: $C_2 > C_3 > C_4 >$ Ph $> i\text{-}C_4 > t\text{-}C_4$. As far as factor (d) is concerned, only $n$-butyrophenone presents a reasonable case for hydrogen bonding, and so, if the bond or a tendency thereto does exist, its carbonyl group will be more easily polarized and therefore more easily reduced.

Only benzophenone and $n$-butyrophenone are out of place in comparing the above orders of reducibility to the observed order. The anomalous character of $n$-butyrophenone is not entirely unexpected, since the increased ease of reduction due to cyclization tendency has been discussed. The facile reduction of benzophenone suggests that $+I_s$ is the predominant factor and that steric considerations are of minor importance; this viewpoint is interesting but cannot be maintained on the basis of the above observations alone, since no attempt has been made to determine the steric effects of the transition state which in the final analysis are probably the determining factors.

## Consideration of Ashworth's Mechanism

Since Ashworth's mechanism[6b] for ketone reduction at the D.M.E. has been accepted by many workers in the area, its defects from the present authors' viewpoint will be considered in some detail.

Ashworth postulates a two-step process in acidic media: reversible formation of a carbonium ion, which is reversibly reduced to a carbinol-free radical

$$RR'C{=}O + H^+ \rightleftarrows RR'C^+{-}OH \qquad (1)$$

$$RR'C^+{-}OH + e^- \rightleftarrows RR'C^0{-}OH \qquad (2)$$
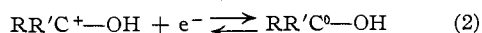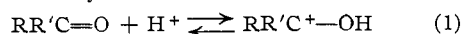
However, the experimental observations negate the possibility of a carbonium ion reduction as the cause of wave I (acidic media). The insensitivity of $E_{1/2}$ to ionic strength variation contradicts the existence of a charged diffusing species. The strong $p$H-dependence indicates electron transfer and proton pickup to be simultaneous. If a carbonium ion were the reducible species, the wave height should be exceedingly small, since the equilibrium of reaction 1 would be almost entirely to the left, carbonium ions being short-lived. Finally, if the reducible species were formed by a reaction in solution, the wave would be kinetically rather than diffusion controlled.

The present authors agree with Ashworth in respect to the origin of wave II (acidic media), i.e., reduction of free radical to carbinol, and the mechanism of the merger of waves I and II to form the combined wave.

The behavior of the combined wave and the tendency of some aromatic ketones to resist combined wave formation have led to some apparently doubtful speculation.[6b,e,20] Ashworth's observa-

(20) (a) R. A. Day, Jr., and R. E. Biggers, This Journal, 75, 738 (1953); (b) R. A. Day, Jr., and W. A. Blanchard, ibid., 76, 1166 (1954).
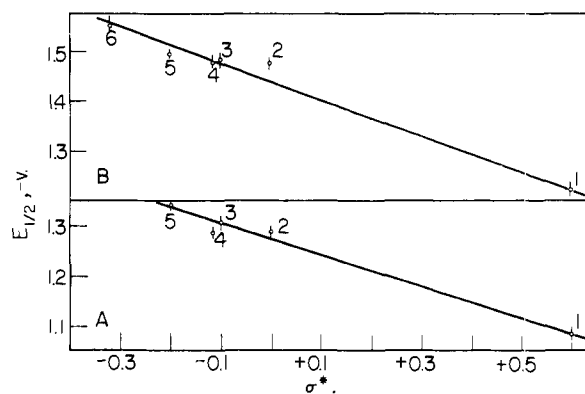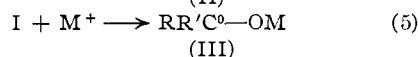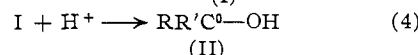


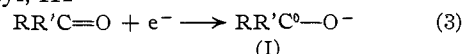Fig. 6.—Correlation of $E_{1/2}$ of the phenyl ketones with polar substituent $\sigma$-values, $\sigma^*$: (A) acetate buffer, $p$H 5; (B) ammonia buffer, $p$H 9. R in R–Y, where Y is $C_6H_5$-CO-, is indicated by the numerals 1 to 6, which stand for phenyl, methyl, ethyl, $n$-propyl, isopropyl and $t$-butyl, respectively.

tions[6b] on the combined wave led him to postulate the so-called *metal ketyl mechanism*, which tacitly assumes the behavior of metal ketyls under polarographic conditions in aqueous solution to be analogous to their behavior in inert solvents. This assumption seems unreasonable *per se* and, as subsequently shown, is not supported by the data.[6b] Specifically, Ashworth assumed that in alkaline media the ketone is reduced directly to the carbinolate free radical ion, I, which reacts with protons and metal ions to form a carbinol free radical, II, and a metal ketyl, III

$$RR'C{=}O + e^- \longrightarrow RR'C^0{-}O^- \qquad (3)$$
$$\text{(I)}$$

$$I + H^+ \longrightarrow RR'C^0{-}OH \qquad (4)$$
$$\text{(II)}$$

$$I + M^+ \longrightarrow RR'C^0{-}OM \qquad (5)$$
$$\text{(III)}$$

II is further reduced to carbinol at the same $E_{1/2}$ while III dimerizes to a greater or lesser degree depending on the nature of the cation. The dimerized and residual monomeric metal ketyls are not reducible at this potential; III is reduced at more negative potential, giving rise to wave III observed above $p$H 9.

This mechanism is partly correct in the sense that the shortage of protons negates the possibility that all of the ketone is reduced with their aid. However, the continued $p$H-dependence of the combined wave is ample evidence that some of the ketone is still being reduced through the mechanism operative in acidic media (Fig. 4, b and c). The portion of ketone not reduced through the protonated transition state is, however, reduced to I. Formation by I of a metal ketyl in a predominantly aqueous environment is unlikely, since alcohols have very little tendency to ionize in aqueous solution; I would preferentially extract a proton from the solvent to form much more stable II rather than the very unstable III. Since I is not reducible at $E_{1/2}$ of the combined wave, it diffuses away from the electrode and so is not available for reduction to carbinol even after extracting a proton from the solvent. In addition, some of the free radical ions tend to dimerize (Fig. 5).

Ashworth assumed that, since pinacols are not polarographically reducible, wave III is not due to pinacol and the decrease in combined wave height cannot be due to its formation. Although pinacol is not the cause of wave III, the present authors have isolated pinacol as the major reduction product above $p$H 9, showing that pinacol formation does account for the decreased combined wave height, i.e., the ketone is being reduced to both carbinol and carbinolate free radical ion, and a considerable portion of the latter is dimerizing both before and after proton pickup.

Further evidence against the metal ketyl mechanism can be gleaned from Day, et al.,[6d,e,20] who found that by increasing ketone concentration and/or decreasing alkali (base) concentration, wave III would appear. This can be interpreted to mean that as long as the ketone concentration is not unfavorably high in relation to that of hydrogen ion, II is formed and reduced, and that metal ketyl formation is not favored by high alkali metal concentration (NaOH used to obtain $p$H 12 to 13).

Wave III, attributed to reduction of III by Ashworth, has been shown in the present study to result from reduction of I. Wave III behavior is consistent with that of an anionic species, e.g., shift to less negative potential with increased ionic strength.[21] Unfortunately, this factor was not considered by Ashworth, who also failed to notice that at a fixed alkali metal concentration, i.e., at essentially the same ionic strength, the effect of the various cations on $E_{1/2}$ was contrary to that expected from electronic considerations; specifically, $E_{1/2}$ becomes increasingly more negative as the atomic number decreases (cesium to lithium). The reverse order would be expected if an intermediate of the type RR'C⁰—OM were involved, since the electron affinity increases with decrease in atomic number, thereby facilitating electron transfer at the electrode.

The possible capillary-active effect of the metal cations was not considered by Ashworth. Lothe and Rogers[22] have pointed out that on the negative side of the electrocapillary curve, capillary-active cations would facilitate reduction since they would produce a potential drop at the electrode. In part, this might account for some of the shifts which Ashworth attempted to explain by the metal ketyl mechanism.

## Polarographic Determination of Ketones

The $E_{1/2}$ and $I$ data summarized in the test and, more particularly, in Figs. 1 to 3 should enable one to select the optimum $p$H for the polarographic determination of a ketone from the viewpoints of securing a single unequivocal wave or one free from interference by the polarographic waves of other substances present and of obtaining a wave with a maximum $I$ value.

## Experimental

**Chemicals.**—Eastman Kodak white label grade acetophenone, $n$-butyrophenone, isobutyrophenone and benzo-

phenone were used without further purification. Propiophenone (Kodak white label grade) and pivalophenone, kindly donated by Dr. P. A. S. Smith, were purified by vacuum fractionation through a $1 \times 28$-cm. helices-packed column; physical constants of the products were: b.p. $114°$ (28 mm.) and $n^{25}$D 1.5245 for propiophenone, and b.p. $119°$ (26 mm.) and $n^{25}$D 1.5091 for pivalophenone. Buffer solutions (Table IV) were prepared from analytical reagent grade chemicals. The nitrogen used for deoxygenating was purified and equilibrated by bubbling it successively through sulfuric acid, alkaline pyrogallol solution, distilled water and, finally, a portion of the test solution.

TABLE IV

COMPOSITION OF BUFFER AND BACKGROUND SOLUTIONS[a]

| Buffer no. | $p$H | Composition |
|---|---|---|
| 1 | 3.8–5.7 | NaOAc + HOAc |
| 2 | 3.0–8.0 | $Na_2HPO_4 \cdot 7H_2O$, citric acid monohydrate + KCl |
| 3 | 8.1–9.7 | $NH_4Cl + NH_3$ |
| 4 | 9.7–12.4 | $Na_2HPO_4 \cdot 7H_2O + NaOH$ |
| 5 | 9.2–9.9 | $Na_2B_4O_7 \cdot 10H_2O + NaOH + KCl$ |
| 6 | 11.0–12.5 | NaOH + KCl |

[a] Buffer solutions were used at an ionic strength of 0.45 $M$ unless otherwise indicated.

**Apparatus.**—Potential–current curves for all ketones except isobutyrophenone and pivalophenone were obtained with a Sargent Model XXI Polarograph; initial and final potentials were measured potentiometrically. A Leeds & Northrup Type E Electro-Chemograph was used to obtain data on isobutyrophenone and pivalophenone and for checks on the other ketones. Capillaries (Corning marine barometer tubing) had $m$ values in mg./sec. and drop-times, $t$, in sec. (distilled water, open circuit) as follows: (A) 1.172, 5.48 ($h = 60$ cm., $25°$); (B) 1.071, 5.94 and 1.670, 3.70 ($h = 50$ and 75, $0°$); (C) 1.106, 5.72 ($h = 60, 25°$); (D) 1.05, 5.82 ($h = 60, 25°$); (E) 1.271, 5.01 ($h = 60, 25°$); and (H) 0.952, 5.97 ($h = 60, 25°$). The heights given are not corrected for back-pressure; however, they were corrected in determining the relation of $i_1$ to $h$. A water-jacketed H-cell[23a] was used at $25°$ and an unjacketed H-cell[23b] at $0°$; each contained a saturated calomel electrode in one arm. The cell solution resistance, measured with a General Radio Type 650A impedance bridge, was below 400 ohms at all times. A Beckman Model G $p$H meter was used for $p$H measurement. All measuring apparatus was calibrated.

A modified Lingane coulometric apparatus[24] was used with a water-jacketed electrolysis ($25.0 \pm 0.1°$) and an external working silver anode. In the macroscale electroreductions, the gas coulometer was by-passed.

**Polarographic Procedure.**—Stock solutions (2.61 to 1.08 $mM$ in ketone) were prepared by dissolving weighed amounts of the ketones in 95% ethanol. The test solution, prepared by pipetting 5.00 ml. of stock solution into a 50-ml. volumetric flask and diluting with buffer solution, was deoxygenated in the cell for 10 min. and then electrolyzed under a nitrogen atmosphere. The potentials reported are corrected for $iR$ drop and are vs. S.C.E.

All polarographic and coulometric test solutions contained 9.5% ethanol (19% in the case of benzophenone) and had a calculated ionic strength of 0.45 $M$, unless otherwise indicated; the presence of the ethanol casts some doubt on the absolute validity of the $p$H measurements reported. In the case of benzophenone, a maximum which appeared above $p$H 8 interfered with the combined wave; however, it was satisfactorily suppressed by making the test solution 0.002 to 0.003% in gelatine.

**Coulometric Procedure.**—Enough mercury to form a cathode area of ca. 25 cm.² and the background electrolyte solution (90 ml. of buffer solution, 0.5 $M$ in ionic strength) were added to the electrolysis cell. While oxygen was removed, the gas coulometer was conditioned. The stirrer with one-half of its blade immersed in the mercury pool was then started, and the tips of the bridges of the reference

(21) P. J. Elving, I. Rosenthal and M. K. Kramer, THIS JOURNAL, 73, 1717 (1951); P. J. Elving, J. C. Komyathy, R. E. Van Atta, C. S. Tang and I. Rosenthal, Anal. Chem., 23, 1218 (1951).

(22) J. J. Lothe and L. B. Rogers, J. Electrochem. Soc., 101, 264 (1954).

(23) (a) J. C. Komyathy, F. Malloy and P. J. Elving, Anal. Chem., 2, 431 (1952); (b) J. M. Markowitz, M.S. Thesis, The Pennsylvania State University, 1952, p. 16.

(24) J. J. Lingane, THIS JOURNAL, 67, 1916 (1945).

and silver anode electrodes were adjusted so that they nearly touched the stirred mercury. The coulometer was then connected in series with the cell and the solution electrolyzed at a cathode potential 0.3 to 0.4 v. more negative than that at which the determination was to be run. This preliminary electrolysis, which removed traces of reducible impurities from the solution, was discontinued when the current became negligible. After a few minutes, the current usually decreased to 1 ma. or less.

The applied potential was then reduced until the cathode potential reached the desired value. The electrical circuit was opened; 10 ml. of stock solution, containing 0.5 millimole of ketone in 95% ethanol, was added; the test solution was deoxygenated for 5 min.; the coulometer buret was read; and the run was started. The applied potential was controlled manually to maintain the desired cathode potential until the electrolysis was complete, *i.e.*, the current was 1 ma. or less. In some cases, the current did not drop below 2 ma.; this was due to incomplete reduction, since some of the reducible material was occluded by the resinous by-product previously mentioned, from which it was apparently very slowly released.

**Macroscale Electrolysis.**—In a typical experiment 2.00 g. (0.0148 mole) of propiophenone was reduced in a manner similar to that used in the coulometric runs at an $E_{max}$ of 1.35 v. *vs.* the S.C.E., except that the ketone was added in small amounts over a period of *ca.* 10 hr. to the deoxy-

genated and conditioned base electrolyte (100 ml. of pH 4.8 acetate buffer containing 9.5% ethanol). After reduction was essentially complete, the electrolyzed solution was extracted with ether; the ether extract was washed with water, dried over anhydrous sodium sulfate and filtered. Ether, any residual unreduced ketone and any carbinol formed were removed by distillation at atmospheric pressure; the oily yellow residue obtained gave white crystals after cooling for an hour at room temperature. The crystals, purified by washing with petroleum ether, were identified as propiophenone pinacol, m.p. of 132°.[12]

Acetophenone (2.00 g., 0.0166 mole) was electrolyzed under the same conditions except that all of the ketone was added at one time to the deoxygenated and conditioned base electrolyte. The reaction mixture obtained was acidified with hydrochloric acid and steam distilled. The residue was extracted with hot benzene; the extract was washed with water, dried over anhydrous sodium sulfate, filtered, concentrated and then diluted with three parts of Skellysolve B. On cooling this mixture in an ice-bath, acetophenone pinacol crystallized out, m.p., 120.5–121.5°.

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# Centrifugal Electromotive Force: The Transference Numbers of Lithium, Rubidium and Cesium Iodides. The Iodide–Iodine Complex[1,2]

BY B. ROGER RAY, DONALD M. BEESON AND HAROLD F. CRANDALL

Measurements have been made of the potentials developed in a centrifugal field by galvanic cells of the type (Pt); $I_2$, MI, $I_2$; (Pt) in which the two otherwise identical electrodes are at different radii. Lithium, rubidium and cesium iodides, approximately 0.2 N, were investigated at 25° over a range of iodine concentrations. The data yielded the following values of the Hittorf transference numbers: $t_{Li} = 0.317$, $t_{Rb} = 0.506$, $t_{Cs} = 0.496$. Utilizing conductivity data, the results are interpreted quantitatively by the previously proposed cell mechanism based upon the presence of the triiodide ion. The partial atomic volumes of the iodine at 25° were found to be 29.82, 30.30 and 30.29 ml./g., at near zero concentration, in solutions of the three iodides.

The simplest type of galvanic cell consists of two identical electrodes immersed in the electrolyte. Examples are M; MX; M, where M is a metal and MX is a salt of the metal, and (Pt); $I_2$, MI, $I_2$; (Pt), where MI is an iodide. Such a cell, if reversible and of uniform concentration and temperature throughout, will have no potential unless, as Des Coudres[3] showed, it is placed in a centrifugal field, whereupon a very small e.m.f. develops. Tolman,[4] working with iodide–iodine type cells, achieved the first quantitative results. More recently, Grinnell and Koenig[5] have measured accurately the closely analogous gravitational e.m.f. of the KI–$I_2$ cell. The latest studies, utilizing improved centrifugal apparatus and techniques, have been carried out by MacInnes and co-workers[6,7] on KI and NaI solutions. Among other things, the work has now

shown that centrifugal e.m.f. data are capable of yielding accurate transference numbers and promise to furnish a method applicable to systems in which the established methods are inadequate.

For the iodide–iodine type cell we have the equation

$$-EF = 2\pi^2 r^2 (x_2^2 - x_1^2) [t_M(M_{MI} - \bar{V}_{MI}\rho) - (M_I - \bar{V}_I\rho)] \quad (1)$$

Here $E$ is the centrifugal e.m.f., $F$ is the faraday, $r$ is the revolutions per second, $x_1$ and $x_2$ are the electrode distances from the center of rotation, $t_M$ is the transference number of the monovalent metal ion, $M_{MI}$ and $\bar{V}_{MI}$ are the molecular weight and partial molal volume of the salt, $M_I$ and $\bar{V}_I$ are the atomic weight and partial atomic volume of iodine and $\rho$ is the density of the solution. This equation states that per faraday of electricity through the cell $t_M$ equivalent of salt is transported from the anode region to the cathode region and one equivalent of iodine in the reverse direction.

If, however, the iodine present in the solution complexes to form an $I_{j+1}$ ion, where $j$ is the number of atoms of uncharged iodine per ion, then the applicable equation is

$$-EF = 2\pi^2 r^2 (x_2^2 - x_1^2) [t_M(M_{MI} - \bar{V}_{MI}\rho) - (1 + jt_c)(M_I - \bar{V}_I\rho)] \quad (2)$$

(1) A portion of the data was taken from the Ph.D. thesis of D. M. Beeson submitted to the Graduate College of the University of Illinois, 1952.

(2) This work was supported by grants from the American Philosophical Society, the Research Corporation and the National Science Foundation. It is a pleasure for the University and the authors to acknowledge this generous assistance.

(3) Th. Des Coudres, *Ann. Physik.* **49**, 284 (1893).

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(6) D. MacInnes and R. Ray, *ibid.*, **71**, 2987 (1949).

(7) D. MacInnes and M. Dayhoff, *J. Chem. Phys.*, **20**, 1034 (1952).