the maleic acid monomer should show considerable ion-bonding. For, for the case of maleic acid, $pK_1 = 1.921$, $pK_2 = 6.225$ and the calculated interaction energy between two charged groups, x, is $8.22RT$ after correction for the statistical factor. If it is further assumed that the mechanism of dissociation of a carboxyl group is the same as the mechanism of association of a counter ion, the ratio of the dissociation constants of the primary and secondary ion pairs would be

$$\frac{K_{s_2}{}^0}{K_{s_1}{}^0} = 2.5 \times 10^{-4} \qquad (25)$$

Therefore, even if the dissociation constant of the primary ion pair is large (as large as in the case of 1:1 electrolytes $\sim 10^2$–10^3), the dissociation constant of the secondary ion pair would be relatively small. If $K_{s_1}{}^0$ were 10^2, $K_{s_2}{}^0$ would be 0.025 and there would be appreciable ion pairing. However if $K_{s1}{}^0$ were 10^3, there would be negligible ion pairing. As shown in Fig. 5, the measured ion-binding of the maleic acid monomer at 95% neutralization is indeed negligible. It is, in any event, likely that the ion-pair in a simple electrolyte solution is entirely different from the "undissociated molecule" pictured in the dissociation equilibrium description. From the physical point of view the major characteristic of the ion pair lies in the assumption (or definition) that the ion-pair has no electrostatic influence on other ions. Therefore, the present experimental results which show that the effect of the non-uniform distribution of fixed charges (and in particular the effect of the nearest neighboring charge) is less important for ion-binding than for the dissociation of the carbonyl group is not unexpected. However, this result does not necessarily mean that there is no site-binding in polyelectrolyte solutions. Since the ions attracted to the neighborhood of the fixed charges by the strong electrostatic field shield the fixed charges and these shielded charges have little or at least lessened electrostatic effect on other charges, the notion of site-binding is useful for explaining many polyelectrolyte phenomena. In this context, the interpretation of site-binding is closely related to the interpretation of the depression of the counter ion activity coefficient. The difference in description is primarily a difference in language.

We believe the most important result of these experiments to be the demonstration of the comparable importance of the near neighbor electric field and the domain electric field. This result clearly calls for a re-examination of the current approximate polyelectrolyte theories, a problem we shall examine in a subsequent publication.

V. **Acknowledgments.**—We wish to thank Miss Winifred Huo for assistance with preliminary measurements and Professor A. E. Woodward of the Pennsylvania State University for an informative exchange of letters. We also wish to thank the National Science Foundation for financial support through NSF G5117.

[CONTRIBUTION FROM THE UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN, AND THE PENNSYLVANIA STATE UNIVERSITY, UNIVERSITY PARK, PENNSYLVANIA]

Polarographic Behavior of Alkyl Phenyl Ketones with Nuclear and Side-chain Halogen Substituents

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Several alkyl phenyl ketones with chlorine and bromine substituted on the benzene ring and/or on the alkyl group have been examined polarographically to determine the effect of structure on the carbonyl group and carbon–halogen bond reductions and to obtain further information on the mechanism for the latter process. Nuclear halogen substitution facilitates carbonyl group reduction, although not in the manner expected from a consideration of inductive effects; it has no apparent effect on the fission of side-chain halogen. Addition of halogen on the side chain has no effect on carbonyl group reductions since the carbon–halogen bond is ruptured at a more positive potential. In the acidic region, *e.g.*, below *p*H 3.5, fission of the C–Cl bond is facilitated by increasing hydrogen ion concentration; this dependence probably is due to the role of hydrogen ion in a push-pull mechanism at the electrode, which is likely accentuated by the decreased dissociation of hydrogen chloride in the 9.5% ethanol solutions used.

Continuing the systematic investigation of electrochemical carbon–halogen bond fission in organic compounds,[1] a series of haloacetophenones, *i.e.*, phenacyl halides, and nuclear halogenated acetophenones and phenacyl halides, have been studied.

The following general characteristics of carbon–halogen bond fission can be deduced from the behavior of substituted aliphatic and aromatic carboxylic

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(1) (a) P. J. Elving, *Record Chem. Progr.*, **14**, 99 (1953); P. J. Elving and C. E. Bennett; (b) *Anal. Chem.*, **26**, 1572 (1954); (c) *J. Electrochem. Soc.*, **101**, 520 (1954); (d) THIS JOURNAL, **76**, 4473 (1954); (e) P. J. Elving and C. M. Callahan, *ibid.*, **77**, 2077 (1955); (f) P. J. Elving and C. L. Hilton, *ibid.*, **74**, 3368 (1952); (g) P. J. Elving, J. C. Komyathy, R. E. Van Atta, C.-S. Tang and I. Rosenthal, *Anal. Chem.*, **23**, 1218 (1951); (h) P. J. Elving and J. T. Leone, THIS JOURNAL, **79**, 1546 (1957); (i) **80**, 1021 (1958); (j) P. J. Elving, J. M. Markowitz and I. Rosenthal, *J. Electrochem. Soc.*, **101**, 195 (1954); (k) P. J. Elving, I. Rosenthal and M. K. Kramer, THIS JOURNAL, **73**, 1717 (1951); (l) P. J. Elving, I. Rosenthal and A. J. Martin, *ibid.*, **77**, 5218 (1955); P. J. Elving and C.-S. Tang, (m) *Anal. Chem.*, **23**, 341 (1951); (n) THIS JOURNAL, **72**, 3244 (1950); (o) *ibid.*, **74**, 6109 (1952); P. J. Elving and R. E. Van Atta, (p) *Anal. Chem.*, **27**, 1908 (1955); (q) *J. Electrochem. Soc.*, **103**, 676 (1956); (r) I. Rosenthal, C. H. Albright and P. J. Elving, *ibid.*, **99**, 227 (1952); (s) I. Rosenthal and P. J. Elving, THIS JOURNAL, **73**, 1880 (1951); (t) I. Rosenthal, J. R. Hayes, A. J. Martin and P. J. Elving, *ibid.*, **80**, 3050 (1958); (u) I. Rosenthal, C.-S. Tang and P. J. Elving, *ibid.*, **74**, 6112 (1952).

TABLE I

SUMMARY OF POLAROGRAPHIC DATA FOR NUCLEAR AND SIDE-CHAIN HALO-SUBSTITUTED ACETOPHENONES

pH	Acetophenone[a]		4'-Chloroacetophenone[a]		4'-Bromoacetophenone[a]		2',5'-Dichloroacetophenone[a]		2-Bromoacetophenone[c,d]		2-Bromo-4'-chloroacetophenone[c,d]		2,4-Dibromoacetophenone[c,d]		2-Chloroacetophenone[a]	
	$-E_{1/1}$	I	$-E_{1/2}$	I	$-E_{1/2}$	I	$-E_{1/2}$	I	$-E_{1/2}$	I	$-E_{1/2}$	I	$-E_{1/2}$	I	$-E_{1/2}$	I
3.2					I 1.09 II 1.28	2.2 2.5									I 0.50[f] II 1.22	3.3 2.6
4.0–4.1	1.23	1.4			I 1.16 II 1.28	1.6 1.6	1.13[b]	3.1							I 0.58 II 1.26	2.7 2.1
4.6–5.0	1.27	1.6	I 1.20 II 1.31	1.4 1.4	1.24[b]	3.4	1.14	3.1	I 0.04 II 1.29	1.5 1.1	I 0.03 II 1.24[b]	0.9 1.3	I 0.02 II 1.22[b]	0.9 1.4	I 0.60[f] II 1.30	3.2 2.4
5.6–5.8	1.34	1.8	1.30	2.8	1.28	3.3	1.17	3.0	I 0.09 II 1.38	1.1 1.2	I 0.08 II 1.29	0.9 1.4	I 0.07 II 1.26	0.9 1.5	I 0.54[f] II 1.36	3.1 2.8
7.0–7.2	1.49	3.2			1.34	2.9	1.25	3.0	I 0.16 II[e] 1.43	0.9 1.8	I 0.17 II 1.37	1.0 1.2	I 0.17 II 1.33	0.8 1.4	I 1.54 II 1.45	2.9 4.0
8.2–8.4	1.45	3.2	1.39	3.4	1.38	3.7	1.27	3.3	I 0.23 II[e] 1.47	1.0 2.3	I0.23 II 1.43	0.7 2.1	I 0.22 II 1.40	0.9 1.8	I 0.57 II 1.46	2.8 3.9
8.8–8.9	1.47	3.7							I 0.24 II[e] 1.50	0.5 2.1	I 0.23 II 1.44	0.7 2.0	I 0.21 II 1.41	0.8 2.0	I 0.57 II 1.48	2.9 4.0
9.4	1.49	3.6	1.46	3.3	1.43	3.8	1.32	3.4							I 0.55 II 1.50	2.7 3.9

[a] The data are for runs made at 25°; other runs were made at 0° to determine the effects of temperature. [b] Two waves, which are almost completely merged, were calculated as one wave. [c] The data are for runs made at 0°; comparative runs were made at 25°. [d] All waves for C–Br fission (wave I) gave maxima, which were less pronounced in the 4'-chloro compound and still less in the 4'-bromo compound. [e] These runs gave hydrolysis waves at −1.3 v. [f] These waves exhibited slight maxima.

acids,[1f,j–o,q–u] esters,[1j,l,o,t,u] ketones,[1e,h,i,p,q] aldehydes[1b,c] and alcohols[1d]: (1) the fission is, in effect, a one-step, 2*e* diffusion-controlled process, probably through a free radical and/or carbanion stage[1j,l]; (2) in polyhalomethyl groups, *e.g.*, X_3C- or X_2CR-, fission occurs in a step-wise manner, rupture of the first C–X bond being more facile than that of the remaining C–X bonds with $-CF_3$ being an exception[1h]; (3) the $E_{1/2}$ *vs.* *p*H relationship in *alpha*-halo carboxylic acids is S-shaped in the *p*H region where acid and anion forms coexist and *p*H-independent outside of this region; (4) with the exception of the results reported in the present study and in reference 1h, carbon–halogen bond fission *per se* is *p*H-independent; (5) carbon–halogen bond fission in nuclear substituted aromatic carboxylic acids is more difficult than in *alpha*-halo carboxylic acids (in polyhalogenated aromatic compounds, reduction is stepwise and greatly influenced by the number of halogens present, their orientation and presumably their character).

The present study is concerned with halogenated acetophenones, particularly with fission of the C–X bond in the phenacyl halides, which presents one of the few cases where both C–Br and C–Cl bond fission can be studied in acidic media without the complication of carboxyl ionization. This is readily apparent since acetophenone exists almost exclusively in the keto form[2] and the electron-withdrawal effect of halogen on the methyl group would accentuate this.

Discussion of the Behavior

Illustrative polarographic data for the compounds studied over part of the *p*H range investigated are summarized in Table I.[3]

Halophenyl Methyl Ketones.—In 4'-chloroacetophenone, 4'-bromoacetophenone and 2',5'-dichloroacetophenone only the carbonyl group is reduced, which results in the appearance of two waves below *p*H 4.6, compared to the one wave observable for acetophenone, whose second wave is obscured by buffer discharge. The *p*H-dependence of wave I ($E_{1/2}$ becomes more negative with increasing *p*H) and the *p*H-independence of wave II results in their merger into a *p*H-dependent "combined" wave at *ca.* *p*H 4.6. The ease of reducibility, at a given *p*H, is 2',5'-dichloroacetophenone > 4'-bromoacetophenone > 4'-chloroacetophenone > acetophenone. The carbonyl group reduction in acetophenone becomes more difficult with decrease in temperature; this presumably is true also for nuclear haloacetophenones.

The temperature coefficients of the current were those expected for a diffusion-controlled process. The diffusion current, i_d, of acetophenone shows a bell-shaped variation in the *p*H range of 4 to 12. Between *p*H 4.6 and 9.4, i_d of the halo substituted ketones is independent of *p*H. Below *p*H 4.6 the two haloacetophenone waves each have i_d values approximately equal to one-half the i_d of the "combined" wave observed above that *p*H. The *n* values calculated from the Ilkovic equation[4] are approximately 2 for the "combined" wave over the *p*H range investigated with the exception of acetophenone, for which *n* for the "combined" wave drops down to about 1 above *p*H 10.5; this reduction is characteristic of carbonyl reduction[1i] so that the halo derivatives would also show it above *p*H

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(2) G. E. K. Branch and M. Calvin, "Theory of Organic Chemistry," Prentice Hall, New York, N. Y., 1941, p. 288.

(3) Detailed tables of data are available from the senior author.

(4) Diffusion coefficients for the ketones were estimated from that of *o*-hydroxybenzyl alcohol (0.72×10^{-5} cm.²/sec. in water) by equating the ratio of the cube roots of the molecular volumes to the inverse ratio of the respective diffusion coefficients.

10.5. The single acetophenone wave observed up to *p*H 5.6 and the two waves observed for the halogen derivatives have *n* values of approximately 1. In acetate buffer, 2′,5′-dichloroacetophenone (*p*H 4.1) and 4′-bromoacetophenone (*p*H 4.8) gave two waves, which were almost completely merged.

Phenacyl and *p*-Halophenacyl Halides.—In the cases of phenacyl chloride (2-chloroacetophenone) and the phenacyl bromides (2-bromoacetophenone, 2-bromo-4′-chloroacetophenone and 2,4′-dibromoacetophenone), two cathodic waves appear over the *p*H range studied. Wave I results from carbon-halogen bond fission and wave II from carbonyl group reduction. The normally well-defined second ketone wave was not observed, since the halophenacyl bromides were not studied below *p*H 5. 2,4′-Dibromoacetophenone actually gives three waves in *p*H 5.0 acetate buffer; the second and third waves, as in the case of 4′-bromoacetophenone, almost completely merge.

The C–Cl fission in 2-chloroacetophenone, which is *p*H-independent above *p*H 3.2, becomes strongly *p*H-dependent below this *p*H (Table I). The C–Br fission is also *p*H-dependent in the acidic region; however, since the waves are small and, in addition, complicated by merging with the anodic chloride wave, maxima and hydrolysis (of the C–Br bond), the data are less reliable. In ammonia buffers the waves are complicated by a chloride wave apparently due to some interchange of chloride for bromide in the phenacyl bromides.

In general, $E_{1/2}$ for the carbonyl group reduction corresponds to that of acetophenone, as would be expected, *cf.* the $E_{1/2}$-*p*H relationship for the 2-chloroacetophenone wave II (acetophenone reduction) in Table I. Ionic strength variation has no effect on $E_{1/2}$ of either 2-chloroacetophenone wave, indicating that the diffusing species is a non-ionized and non-protonated species. Both C–Cl bond fission and carbonyl group reduction in 2-chloroacetophenone become more difficult with decrease in temperature.

In acidic media the phenacyl halides, particularly the bromides, give considerable maxima; consequently, it was generally necessary to keep the ketone concentration below 0.14 m*M* in order to obtain calculable curves. Temperature coefficients of I ($i_d/Cm^{2/3}t^{1/6}$) for both 2-chloroacetophenone waves and the variations of i with drop-time (mercury height) indicate that both C–Cl bond and carbonyl group reductions are diffusion-controlled processes. Values of i_d for the carbon-halogen bond fission over the *p*H range at a given concentration are essentially constant; Ilkovic *n* values range from 0.5–1.3 for the C–Br bond fission[5] and are 2 for the C–Cl bond fission.

Values of i_d for wave II increase with increasing *p*H in much the same manner as described for acetophenone with apparent Ilkovic *n* values for ketone reduction increasing from about 0.71 to 1.45 in the bromides and from 1.11 to 2.5 in 2-chloroacetophenone.

Both 2-chloroacetophenone waves vary linearly with concentration.

Anomalous Behavior of Phenacyl Bromides.—In contrast to 2-chloroacetophenone, the phenacyl bromides give indications of additional waves in both acidic and alkaline media, particularly when electrolyzed at 25°. These additional waves are due to hydrolysis products, especially in alkaline media, and to possible exchange reactions.[6] The latter are of little consequence in the present study since the solutions were examined immediately after being prepared. Although irregularities were noted at the potentials where an exchange by-product (2-acetoxyacetophenone or 2-chloroacetophenone) would be expected to be reducible, there were no cases where a measurable wave actually developed.

Electrolysis of one possible exchange by-product, 2-acetoxyacetophenone (Table II), gave two well-defined cathodic waves in acidic media and three such waves in alkaline media. Wave I in acidic media (fission of the C–OAc bond) has an $E_{1/2}$ approximately equal to the potential at which irregularities had been observed in reduction of the bromides in acidic media (0.9–1.1 v.); wave II is due to reduction of acetophenone produced from the C–OAc bond fission.

There was some indication that chloride exchange occurred in ammonia buffers, *e.g.*, slight irregularities appeared in the region of 0.55–0.65 v., which corresponds to the $E_{1/2}$ of C–Cl bond fission in 2-chloroacetophenone.

The height of wave I produced by 2-acetoxyacetophenone electrolysis in alkaline media was greatly diminished by formation of a hydrolytic by-product, whose reduction at a slightly more negative potential gives rise to wave II; the sum of these two waves equals the height of the first wave observed in acidic media. Polarographic studies of 2-hydroxyacetophenone verified that the hydrolytic wave is indeed due to C–OH fission in 2-hydroxyacetophenone. As expected, the third wave corresponds to that of acetophenone.

It is apparent that in the study of labile compounds of the phenacyl type, particularly bromides and, presumably, iodides, care must be taken to avoid possible exchange and hydrolysis reactions. If measurements are made immediately on preparation of the test solution and at reduced temperature, exchange reactions can be ignored and hydrolysis can be minimized.

Effect of Substitution on Reducibility.—Nuclear substitution of halogen in a phenyl ketone profoundly affects the reactivity of the carbonyl group, causing a remarkable increase in its ease of reduction, which for the compounds studied at a given *p*H, temperature and solution environment is 2′,5′-dichloroacetophenone > 4′-bromoacetophenone > 4′-chloroacetophenone > acetophenone. As expected from the reaction paths, wave II in the phenacyl halides shows the same trend for the ease of reduction (species actually being reduced is

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[5] These figures represent, at best, a poor approximation, since the diffusion coefficient *D* for the bromides were estimated from that of *o*-hydroxybenzyl alcohol at 25° and then corrected to 0°, assuming the temperature coefficients of the bromides would be the same as that of phenacyl chloride. Obviously, hydrolysis, exchange reactions and possible non-linearity of i_d with concentration in the solutions used would tend to give low *n* values.

[6] H. H. Pokras and H. I. Bernstein, THIS JOURNAL, **65**, 2096 (1953).

given in parentheses): 2,4′-dibromoacetophenone II (4′-bromoacetophenone) > 2-bromo-4′-chloroacetophenone II (4′-chloroacetophenone) > 2-bromoacetophenone II (acetophenone).

TABLE II

SUMMARY OF POLAROGRAPHIC BEHAVIOR OF 2-ACETOXYACETOPHENONE AND 2-HYDROXYACETOPHENONE[a]

Compound	*p*H	Wave I $-E_{1/2}$	Wave I I	Wave II $-E_{1/2}$	Wave II I	Wave III $-E_{1/2}$	Wave III I
2-Acetoxy	5.6	0.97	3.2	1.35	1.8		
	9.4	1.12	1.8	1.34	1.4	1.50	2.1
2-Hydroxy	4.6	1.10	2.3	1.30	0.8		
	9.2	1.34	1.7	1.50	0.5		

[a] Data given obtained at 25°.

Nuclear substitution has no noticeable effect on the ease of reduction of the alkyl group carbon–bromine bond. This is not entirely unexpected since the C–X bond is two carbon atoms from the benzene nucleus and therefore the inductive effect $+I_s$, of the nuclear halogen substituents is considerably weakened. Another factor is the extreme facility of C–Br bond fission in the phenacyl compounds; even though the nuclear substituents might facilitate the reduction, the change would be small and, in view of the susceptibility of the bromides to side reactions, hardly noticeable.

The order of reducibility observed for the nuclear halo acetophenones is not in agreement with that which would be expected from a consideration of permanent polarization effects (the inductive effect, $+I_s$), *e.g.*, 4′-chloroacetophenone should be more easily reduced than 4′-bromoacetophenone. A possible explanation for the observed trend is that bromine, due to its deformability, is polarized in the field of the electrode and thereby aids in the reduction by becoming a quasi electron sink. The net result would be that polarization of the bromine supplements its $+I_s$, giving a greater total electron-withdrawing force than that of chlorine.

The easier reduction of 4′-bromoacetophenone as compared to 4′-chloroacetophenone is in line with Ingold's inductometric effect.

Mechanism.—The fission of carbon–halogen bonds at the d.m.e. can follow two possible reaction schemes[1a,j,l]: (1) S_N2, *i.e.*, formation of an electrode complex followed by back-side addition of two electrons and simultaneous dissociation of the C–X bond with a subsequent rapid acquisition of a proton from the solvent and (2) free radical, *i.e.*, acquisition of an electron simultaneous with C–X bond fission followed by the rapid acquisition of a second electron by the free radical and subsequent proton pickup.

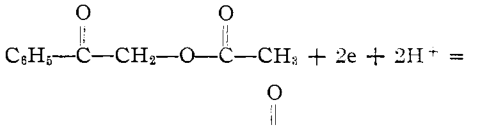
The S_N2 mechanism has not only been able to explain satisfactorily C–X bond fission in the haloalkanoic acids but also in the phenacyl halides. The free radical mechanism also fits the observed behavior of C–X bond fission, but no conclusive evidence has yet been found for the existence of an alkyl free radical which would be the transition state species. Corroborative evidence for a free radical mechanism has been found in the reduction of bromomaleic acid[1a] which yields some butadiene tetracarboxylic acid as one of the reduction products. An additional point becomes apparent if one considers the actual probability of the simultaneous transfer of an electron pair (S_N2 mechanism) or successive addition of single electrons (free radical mechanism); successive electron addition is certainly the more logical process.

In the region where C–Cl bond fission is *p*H-dependent (below *p*H 3.2), hydrogen ion obviously enters into the electrode process, which can be depicted as the result of a concerted push-pull attack on the C–Cl bond by both the electrode and hydrogen ion. As the concentration of hydrogen ion increases, so does its contribution to the energy needed for rupture of the C–Cl bond, *i.e.*, the greater the tendency for hydrogen ion to associate with chlorine, the lesser the amount of energy the electrode need provide to bring about the bond fission. Confirmatory evidence for such a process is seen in the C–F bond fission in phenacyl fluoride (2-fluoroacetophenone).[1h] In the present study, the *p*H-dependence of C–Cl fission may have been accentuated by the decreased dissociation of HCl in the 9.5% ethanol solutions used. A similar *p*H-dependence for the C–Br bond fission is less firmly established.

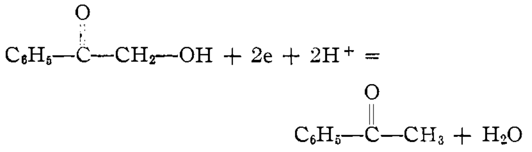
The effect of protonation of the carbonyl group is not in itself sufficient to explain the observed *p*H-dependence, although such protonation may be a contributing factor. If the primary cause of the *p*H-dependence were the protonation of the carbonyl group, one would expect the effect to be more marked in the fission of the carbon–chlorine bond than in that of the carbon–fluorine bond due to the normally greater stability of the latter bond. Actually, the reverse is observed. The *p*H-dependence in the case of C–F bond fission is observed up to *p*H 6, while that in the case of C–Cl bond fission is observed only up to *p*H 3. Furthermore, the *p*H effect in the case of carbon–bromine fission is observed only at still higher acidity. This variation is parallel to the halogen-hydrogen bonding and is opposite to the expected effect of a protonated carbonyl on the fission of the adjacent carbon–halogen bond. Furthermore, if protonation of the carbonyl group were a strong influence, some *p*H-dependence of the $E_{1/2}$ of 2-bromoesters would be expected; actually, none is observed.[1j] Another argument against protonation of the carbonyl group prior to reduction is the lack of variation of $E_{1/2}$ with changing ionic strength.

The ketonic reduction mechanism for the alkyl phenyl ketones has been described in detail.[1i] Essentially, in acidic media (*p*H 5 or less) the ketone is reduced to the corresponding carbinol free radical (*p*H-dependent process), which subsequently dimerizes to the pinacol until its reduction potential is reached, at which time the carbinol free radical is reduced to the corresponding carbinol (*p*H-independent process). In more alkaline media, the ketone is reduced to carbinol free radical, which is immediately reduced to the carbinol at its formation potential (the total process is *p*H-dependent). Above *p*H 9 the amount of carbinol formed decreases while that of pinacol increases, due to the fact that, as the hydrogen ion concentration decreases, less of the ketone is reduced to the carbinol free radical and more to the corresponding free radical ion; since the latter is not reducible at its formation potential, it dimerizes to pinacol. The carbinol free radical ion is itself reducible to carbinol but at a potential slightly more negative than that at which it was formed.[11,7]

The wave pattern for carbon-bromine fission in the phenacyl bromides is complicated by hydrolysis of the C-Br bond, particularly in alkaline media, and by possible exchange with chloride ion in ammonia buffers and with acetate ion in acetate buffers. Study of 2-acetoxyacetophenone, which gives an extra wave in alkaline media (reduction of its hydrolysis product, 2-hydroxyacetophenone), and of 2-hydroxyacetophenone have shown that the hydrolysis product reduced in solutions of phenacyl bromides is the corresponding hydroxyacetophenone; fission of the C-OAc and C-OH bonds occurs to give acetophenone, which is reduced at a more negative potential. The probable over-all electrode reactions for the first wave of each compound are



$$C_6H_5\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}CH_2\text{—}O\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}CH_3 + 2e + 2H^+ = C_6H_5\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}CH_3 + CH_3\text{—}COOH \quad (1)$$



$$C_6H_5\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}CH_2\text{—}OH + 2e + 2H^+ = C_6H_5\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}CH_3 + H_2O \quad (2)$$

Mention has been made of the fact that when a hydroxy or an acetoxy group is present *alpha* to a carbonyl group in a non-conjugated steroid, the former group is reduced prior to the carbonyl group reduction.[8]

Experimental

Chemicals.—Eastman white label grade 2-acetoxyacetophenone, 2-hydroxyacetophenone, 2-chloroacetophenone, 2-bromoacetophenone, 4′-bromoacetophenone, 2′,5′-dichloroacetophenone, 2-bromo-4′-chloroacetophenone and 2,4′-dibromoacetophenone were used. The 2-bromoacetophenone and 2,4′-dibromoacetophenone were recrystallized several times from petroleum ether[9a] and ethyl alcohol,[9b] respectively (m.p.: 2-bromoacetophenone, 49.5–50.5°; 2,4′-dibromoacetophenone, 108.5–110°). Acetophenone (Paragon) was fractionated under reduced pressure (b.p. 81–83° at 10.5 mm.). Mathieson practical grade 4′-chloroacetophenone was used as obtained, since the material was polarographically pure. Buffers (Table III) were prepared from analytical grade chemicals tested for polarographic impurities. Stock ketone solutions were prepared by dissolving a weighed amount of ketone in 95% ethanol shortly before the electrolyses were run.

TABLE III

COMPOSITION OF BUFFER AND BACKGROUND SOLUTIONS[a]

pH	Composition
0.5	Dilute HCl
2.2	HCl + KCl
3.9–5.7	NaOAc + HOAc
3.0–7.2	$Na_2HPO_4 \cdot 7H_2O$, citric acid Monohydrate + KCl
8.2–9.5	$NH_4Cl + NH_3$
9.6–12.3	$Na_2HPO_4 \cdot 7H_2O$ + NaOH

[a] All buffer solutions were used at an ionic strength of 0.45 *M* unless otherwise indicated.

Apparatus.—Potential–current curves were obtained on a Sargent Model XXI Polarograph (initial and final potentials measured potentiometrically) and a Leeds & Northrup Type E Electro-Chemograph. A Beckman Model G pH meter was used for pH measurement. Capillaries (marine barometer tubing, Corning Glass Company) had *m* values (mg./sec.) and drop-times (sec.) in distilled water at open circuit in the ranges of 0.95–1.87 and 3.7–6.0. Two H-cells containing a saturated calomel reference electrode in one arm were used: a jacketed cell[10] maintained at 25.0 ± 0.1° by circulating water from a thermostated bath and an unjacketed cell maintained at 0.0 ± 0.1° by immersion in an ice-bath. The cell resistance, measured with a General Radio Type 650A impedance bridge, was below 400 ohms at all times.

Procedure.—The test solution, prepared by diluting 5.00 ml. of stock solution with buffer in a 50-ml. volumetric flask, was transferred to the polarographic cell, purged with purified and equilibrated nitrogen for 10 min. and then electrolyzed; the nitrogen atmosphere was maintained throughout the electrolysis. Reported potentials are corrected by iR drop and are *vs.* the s.c.e. Currents for second waves are corrected for electrocapillary.

Since all test solutions were 9.5% in ethanol, some doubt exists concerning the absolute validity of the pH measurements reported. The test solution ionic strength for the data in Tables I and II was 0.45 *M;* comparative runs were made at ionic strength levels of 0.90 and 1.80 *M*.

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