[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF EMORY UNIVERSITY]

Some Studies of the Polarography of Aromatic Ketones

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The polarographic reduction of fluorenone, benzophenone, α-benzoylnaphthalene and benzanthrone has been studied in solutions of different ethanol concentrations and at various *p*H values. In acid solution it was found that an increase in ethanol concentration may cause two waves to merge, even at the same apparent *p*H. In alkaline solution an increase in ethanol concentration may change the half-wave potential slightly but not the number of waves observed. The nature of the buffering material in two solutions of the same *p*H affects the half-wave potential slightly, but influences the number of waves observed only in a *p*H region where a change in the number of waves is occurring. In basic solutions of the same composition fluorenone shows the strongest tendency to form double waves, followed by benzanthrone, benzophenone and α-benzoylnaphthalene. This difference in behavior in basic solution has been suggested to be caused by the extent to which the dimerization of a metal ketyl intermediate is influenced by the attached organic radical.

It is well known that the reduction characteristics of ketones, as well as many other organic compounds, at the dropping mercury electrode depend upon such factors as *p*H, concentration of organic solvent in the medium being electrolyzed, type and concentration of buffer used, and many others.[1] In general ketones show a two-step reduction process in acid solution (two waves of about equal height), these waves merging in solutions of higher *p*H. In basic solution usually one wave of full height is observed.

There are many apparent exceptions to the above general behavior. Frequently ketones are found to reduce in one step in fairly acid solution. The single wave in basic solution may split under certain conditions, giving a small second wave at more negative potentials. This tendency of the basic wave to split has been investigated extensively by Ashworth.[2] The ketone fluorenone is of especial interest in its behavior. It has been reported to reduce in two steps of about equal height over the *p*H range of about 1 to 13.[2,3] Ashworth[2] also reported the existence of a small third wave in dilute solutions of alkali hydroxides.

The present study was undertaken to determine what effect, if any, the concentration of organic solvent (ethanol, in this case) has upon the reduction characteristics of benzophenone and fluorenone. Benzophenone generally shows the "normal" behavior described above.[3] Also different buffering materials giving about the same *p*H have been compared in some instances and polarograms have been run at numerous *p*H values in both acidic and basic media. Since under identical solution conditions fluorenone shows a much stronger tendency toward forming double waves than does benzophenone, two other ketones of similarly related structure, benzanthrone and α-benzoylnaphthalene, have been studied. It is hoped that such studies may aid in the formulation of a general mechanism for the reduction of ketones at the dropping mercury electrode.

Experimental

Apparatus.—A few of the earlier current voltage curves were determined using a Leeds and Northrup Electro-Chemograph. Later a new Electro-Chemograph Type E was obtained and most of the data was obtained with this instrument. The instrument was normally operated at a current range of 3 macroamperes and a damping of 3. Half-wave potentials were corrected for lag at this damping, the correction amounting to about 0.056 volt.

The electrolysis cell was the H-type used by Lingane and Laitinen,[4] the anode arm containing a saturated calomel electrode. Two capillaries of Corning marine barometer tubing were used, one in the work with benzophenone and fluorenone, the other with α-benzoylnaphthalene and benzanthrone. The characteristics were: capillary 1, droptime 4.0 sec., m = 1.641 mg./sec; capillary 2, droptime 5.0 sec., m = 1.538 mg./sec. These results were obtained in a 25% ethanol solution of a citrate–phosphate buffer of *p*H 5.0 at −1.00 volt. The resistance of the cell containing solutions of different alcohol concentrations was measured at several *p*H values. A correction for *IR* drop was made when this amounted to as much as 0.01 volt. No attempt was made to correct for liquid junction potential between the ethanol solutions and the saturated potassium chloride in the reference electrode.

The electrolysis experiments with benzophenone and fluorenone were carried out in a thermostat at 25 ± 0.05°. The runs on α-benzoylnaphthalene and benzanthrone were made at room temperature. The temperature was noted during experiments and was usually between 23 and 27°. All volumetric apparatus was checked for correctness of calibration.

Materials and Medium.—Benzophenone and fluorenone were commercial products which were purified by recrystallization. Melting points (uncor.) were: benzophenone 48.5°, fluorenone 83.5°.

The α-benzoylnaphthalene was prepared by Mr. E. R. Covington of this Laboratory according to the method of Fieser.[5] After purification by recrystallization its melting point was 75–76°. The benzanthrone was kindly furnished us by Mr. W. P. Munro of the American Cyanamid Co. It had been recrystallized from monochlorobenzene and had a melting point of 168.5–170°.

Cell solutions were prepared with varying percentages by volume of 95% ethanol. All cell solutions were 0.00025 *M* in ketone unless otherwise noted. To obtain the desired *p*H the following aqueous solutions were used: *p*H 1, hydrochloric acid; *p*H 2 to 8, 0.1 *M* citric acid, 0.2 *M* disodium phosphate; *p*H 4 to 6, 0.1 *M* sodium hydroxide, 0.1 *M* potassium acid phthalate; *p*H 4 to 5.5, 0.1 *M* acetic acid, 0.1 *M* sodium acetate; *p*H 6 to 8, 0.1 *M* sodium hydroxide, 0.1 *M* monopotassium phosphate; *p*H 8 to 10, 0.1 *M* sodium hydroxide, 0.1 *M* boric acid; *p*H 11, 0.1 *M* sodium or lithium carbonate; *p*H 12 to 13, sodium hydroxide. Equal volumes of aqueous buffer and alcoholic solution of the ketone were mixed to form the cell solution.

It was noted that solutions of benzophenone which had stood for some time before use gave unusually large currents in alkaline solutions, particularly in solutions of 40 and 50% ethanol. For this reason all results reported are for solutions prepared within a few hours before use. This effect was not noted with the other ketones except in one instance where a solution of fluorenone had stood for several months.

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[1] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, pp. 343–347.

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

[3] R. A. Day, Jr., and J. J. Kirkland, THIS JOURNAL, **72**, 2766 (1950).

[4] J. J. Lingane and H. A. Laitinen, *Ind. Eng. Chem., Anal. Ed.*, **11**, 504 (1939).

[5] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, pp. 192–193.

Measurements of *p*H were made using a glass electrode and a Beckman Model G or Model H-2 *p*H meter. Measurements were recorded for both the aqueous solutions and the final cell solutions containing alcohol.

Results

It was found in the case of benzophenone in solutions of low *p*H where two waves are observed that the half-wave potential of the first wave is increased (negatively) by an increase in the concentration of ethanol in the solvent. The half-wave potential of the second wave is practically independent of the concentration of ethanol. This is the same general effect that increase in *p*H has upon these potentials, and, as might be expected, a sufficient increase in ethanol concentration leads to a merging of the two waves. It is, of course, difficult to separate the effects of *p*H and alcohol since an increase in alcohol concentration leads to an increase in the apparent *p*H as measured with a glass electrode. However, from the few results given in Table I, it can be seen that while two waves are obtained in a 25% ethanol solution of apparent *p*H 5.1, only one wave (full height) is obtained in 40% ethanol solution of *p*H 4.4. Likewise, the two waves are merged in a 50% ethanol solution even at a *p*H of 3.4. The effect of increased alcohol in such cases may result from a lowering of the true hydrogen-ion activity, not recorded by the usual measurement of *p*H. The equilibrium

$$R_2C{=}O + H^+ \rightleftarrows R_2C^+{-}OH$$

which undoubtedly exists in acid solution, would thus be shifted to the left and the potential for reduction of the carbonium ion would be more negative.

TABLE I

$E_{1/2}$ *vs.* THE SATURATED CALOMEL ELECTRODE (ALL $E_{1/2}$ VALUES ARE NEGATIVE)

*p*H (aq.)	*p*H (alc.)	% alc.	$E^1_{1/2}$	$E^2_{1/2}$	$E^{12}_{1/2}$[a]	$E^3_{1/2}$
			Benzophenone[b]			
3.5	4.0	25	0.99	1.19	..	..
4.6	5.1	25	1.09	1.20	..	..
5.5	6.0	25	..	..	1.19	..
3.5	4.1	30	1.02	1.18	..	..
4.0	4.7	30	1.06	1.19	..	..
4.6	5.2	30	..	..	1.14	..
3.0	3.7	40	1.03	1.19	..	..
3.3	4.0	40	1.06	1.21	..	..
3.7	4.4	40	..	..	1.12	..
2.5	3.4	50	..	..	1.09	..
			Fluorenone[c]			
7.4	8.1	30	0.89	1.02	..	..
7.0	7.9	40	0.90	1.01	..	..
7.4	8.2	40	..	..	0.99	..
5.8	6.8	50	..	..	.98	..
8.0	8.8	30	0.93	1.11	..	1.57
8.8	9.6	30	.97	1.12	..	1.46
9.6	10.3	30	..	..	1.05	1.37
10.0	10.7	30	..	..	1.02	1.34

[a] Indicates $E_{1/2}$ of wave formed by merging waves 1 and 2. [b] All results in citrate–phosphate buffers. [c] First four results in citrate–phosphate, last four in borate buffers.

The behavior of fluorenone in acid solution is similar to that of benzophenone. However, the two acidic waves are more difficult to merge. Even in 50% ethanol the waves are not merged until the *p*H of the cell solution is 6 (acetate buffer). In 40 and 30% solutions these waves are not merged until *p*H values of 9.0 and 10.1 (in borate buffers), respectively, are reached. Also in the 30% ethanol solutions, before these two waves are merged, a third wave at much higher potentials begins to grow in. The growth of this third wave was particularly evident in borate buffers, 30% ethanol, between *p*H values of about 8 to 11. This is shown diagrammatically in Fig. 1. There it can be seen that as the first two waves merge, the third wave grows in height, and its half-wave potential decreases (negatively). In more alkaline solution, the two waves resulting from this transition are usually about equal in height.

In basic solution, under the conditions normally used, only one wave was observed with benzophenone. The half-wave potential continued to shift to more negative values as the *p*H was increased. Other workers[2,3] reported the appearance of a small second wave at high negative potentials in this *p*H range. We were able to observe this small wave by duplicating the solution conditions of the above workers. By changing the concentration of ketone from 0.00025 to 0.001 *M*, or by using more dilute alkali solutions, this second wave would appear. It thus seems that the tendency toward producing this second wave increases as the ratio of ketone to buffer increases. The percentage of ethanol in the solution has only slight effect on the half-wave potentials in the basic region for both benzophenone and fluorenone. No differences in the number of waves were observed with different concentrations of alcohol. The two waves normally obtained with fluorenone, for example, are practically *p*H independent and show no tendency to merge as the ethanol percentage is increased to 50%.

It was also found that changing the nature of the buffer material usually caused a small change in half-wave potential, but normally did not change the number of waves observed. At certain *p*H values, however, where for example the two acid waves are merging, the number of waves may be different for different buffers. Thus fluorenone in 50% ethanol, citrate buffer of *p*H 5.0, gives two waves, but with a phthalate or acetate buffer of *p*H 5.0 gives only one wave of double height. In the *p*H region where the transition from acid to basic mechanism is occurring similar effects were sometimes observed with fluorenone.

The general mechanism proposed by Ashworth[2] for the polarographic reduction of ketones explains satisfactorily the behavior of benzophenone. However, the explanation for the fact that under identical experimental conditions, both in acid and alkaline solutions, benzophenone may reduce in one step and fluorenone in two is not clear. One apparent difference between these two ketones is the nature of the groups attached to the carbonyl, in this case the 9-fluoryl group in fluorenone as compared to two phenyl groups in benzophenone. It is noteworthy that data available on the effect of various groups in promoting free radical stability list the 9-fluoryl group as very ineffective in promoting such

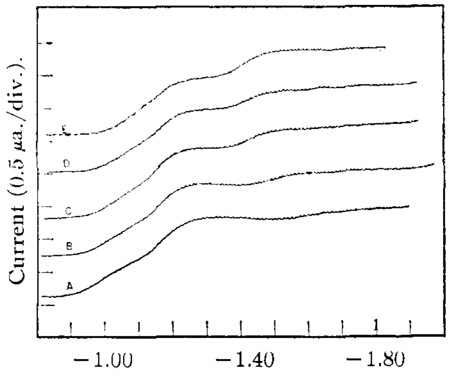

Fig. 1.—2.5 × 10^{-4} *n* fluorenone, borate buffers, 30% ethanol; *p*H (alcoholic): A, 8.8; B, 9.6; C, 10.1; D, 10.3; E, 10.7.

stability, less so than two phenyl groups.[6] If this fact is combined with Ashworth's evidence for increased dimerization of a metal ketyl (assumed as the intermediate in alkaline solution) as leading to the production of a second wave, it is evident that fluorenone should have a greater tendency toward double wave formation than benzophenone regardless of base or metal ion concentration.

To further test the above postulate, two other ketones, α-benzoylnaphthalene and benzanthrone, were studied. The former compound can be regarded as related to benzophenone, with one phenyl group replaced by an α-naphthyl group. The latter group is known to have a greater stabilizing effect on a free radical than the phenyl group.[6] Benzanthrone is similarly related to α-benzoylnaphthalene as fluorenone is to benzophenone; *i.e.*, the phenyl and α-naphthyl groups are joined to form a common ring system as the two phenyl groups are joined in fluorenone. While no experimental evidence is available on the effect of the benzanthryl group in promoting free radical stability, from steric considerations it appears that it would be less effective than the combined effect of a phenyl plus an α-naphthyl group, but probably more effective than a 9-fluoryl group.

Most of the studies made with these two ketones were in 50% ethanol solution. Attempts were made to reduce benzanthrone in solutions of lower ethanol content but the limited solubility of this ketone led to precipitation when the alcohol solution was mixed with aqueous buffer. With α-benzoylnaphthalene only one wave was obtained over the entire *p*H range. This wave has a half-wave potential of −1.17 v. in a 50% ethanol solution of *p*H 4.7, decreases to −1.50 volts at a *p*H of 9.6, and remains about constant in more alkaline solutions. Below an aqueous *p*H of 3.8 previous discharge of hydrogen masked the reduction wave of this ketone. Since the two acidic waves of benzophenone are merged at this *p*H in 50% ethanol, some runs were made in solutions of lower alcohol content. In 25% ethanol at an alcoholic *p*H of 3.5 two waves were obtained of half-wave potentials −1.02 and −1.22 v. These waves were not very sharply defined and were more readily merged than those of benzophenone. In basic media it was found necessary to reduce the metal hydroxide concentration to 0.0001 *M* before a second small wave could be observed. This is considerably lower base concentration than is needed to produce two waves with benzophenone.

Benzanthrone was found to reduce in only one step in acid solution. In a solution of *p*H 1.6 the half-wave potential is −0.54 volt. Presumably the high alcohol content of the solution caused the usual two acid waves to be merged. It should be noted, however, that the two waves of fluorenone did not merge in 50% ethanol until an alcoholic *p*H of 6 to 7 was reached. A second small but poorly defined wave was occasionally observed in acid solution around −1.30 v.

In basic solution at an alcoholic *p*H of 10.4 a small additional wave was apparent at −1.64 v. As the *p*H was increased the half-wave potential of this wave decreased (negatively) and the principal wave began to split. At *p*H 10.7 three waves were present of relative heights 1.0 to 0.43 to 0.10, respectively. In 0.1 *M* sodium carbonate and in 0.1 *M* sodium hydroxide only two waves were present, these being of about equal height in the latter solution. In 0.01 *M* sodium hydroxide all three waves were observed. Since the concentration of sodium hydroxide affected the number of waves observed, several runs were made at different concentrations of base. The results are given in Table II and shown diagrammatically in Fig. 2. Similar results were obtained in dilute solutions of lithium hydroxide and of sodium carbonate.

TABLE II

EFFECT OF NaOH CONCENTRATION ON WAVES OF BENZANTHRONE

NaOH, *M*	$-E^1{}_{1/2}$	$-E^2{}_{1/2}$	$-E^3{}_{1/2}$	Fraction of total current Wave: 1	2	3
0.10	1.14	1.41	..	0.50	0.50	..
.08	1.14	1.43	..	.53	.47	..
.06	1.16	1.42	..	.53	.47	..
.05	1.15	1.39	1.55	.55	.26	0.19
.03	1.15	1.37	1.55	.51	.25	.24
.01	1.16	1.35	1.59	.52	.24	.24
.005	1.16	1.35	1.63	.54	.24	.22

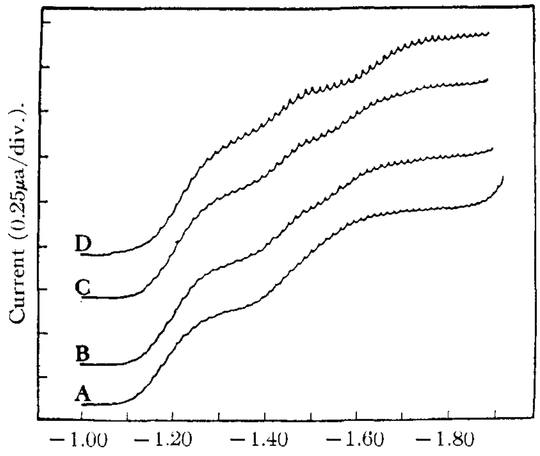

Fig. 2.—Benzanthrone, 50% ethanol: NaOH, *M*; A, 0.10; B, 0.05; C, 0.03; D, 0.01.

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[6] H. Gilman, "Organic Chemistry, An Advanced Treatise," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 591.

Numerous attempts were made to observe the third wave of fluorenone reported by Ashworth[2] as appearing in dilute solutions of alkali hydroxides. Runs were made in solutions as dilute as 0.0001 M in sodium hydroxide, up to 0.001 M in fluorenone, as low as 7.5% in ethanol, and with different degrees of damping, but in no case were we able to obtain a third wave. The half-wave potential of the second wave was shifted to more negative values as the concentration of alkali was reduced. For example in 30% ethanol the values for the two waves were −1.08 and −1.32 v. in 0.1 M NaOH; in 0.005 M NaOH the values were −1.09 and −1.47 v. the values were −1.09 and −1.47 v. The potential of this second wave was also shifted to more positive values by the addition of small amounts of a neutral salt, such as potassium chloride. Ashworth,[2] while pointing out that the third wave observed with fluorenone corresponded to the second wave of benzophenone, listed values of shifts of half-wave potentials of the second wave of fluorenone with change in alkali concentration or concentration of neutral salt.

The over-all behavior of these four ketones as regards double wave formation in basic solution is qualitatively that which one would expect from the tendencies of the groups attached to the carbonyl to increase the stability of a metal ketyl intermediate. Fluorene shows the greatest tendency to form double waves, followed by benzanthrone, benzophenone and α-benzoylnaphthalene. The 9-fluoryl group is least effective in promoting free radical stability, followed by the benzanthryl, phenyl and α-naphthyl groups. It is also true that the same tendency holds in acid solutions, with the possible exception of benzanthrone, which could not be studied in solutions of low alcohol content. In acid solution, however, the dimerization of a free radical is presumably not reversible[7] and leads to the production of a pinacol. The explanation used for basic media would not then be applicable unless one assumes that solution conditions about the mercury drop are considerably different from those existing in usual organic preparative procedures. The fact that the second wave of benzanthrone in basic solution splits more readily than that of fluorenone may be the result of the second step proceeding partly through a free radical intermediate and partly through the metal ketyl.[2] If the dimerization of the metal ketyl alone is influenced by the concentration of alkali, this splitting of the second wave is plausible.

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(7) Ref. 6, p. 612.

EMORY UNIVERSITY, GEORGIA

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF PORTLAND]

Polarographic Reduction of Iodonium Salts

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The polarographic reduction at the dropping mercury cathode of both symmetrically and unsymmetrically substituted iodonium salts is noted and reported. The mercury electrode is apparently involved in the reaction. A mechanism for the three step reduction is proposed in agreement with the experimentally found and derived polarographic data. The effect of buffering, acidity, solvent and concentration are reported in connection with the mechanism and analytical scheme for determining iodonium salts quantitatively.

Reported polarographic studies on positive halogen compounds are scarce and rather incomplete. Heller and Jenkins[1] studied the behavior of hypochlorite and N-chloroamines at the dropping mercury electrode. Their brief report shows an irreversible two electron reduction at +0.08 to −0.13 volt *vs.* S.C.E.

The presently reported investigation deals with the polarographic characteristics of a special series of positive iodine compounds, namely, iodonium salts. The study is restricted to this one member of the halogen family since only in the case of iodine are these dicovalent halogen "onium" compounds stable enough to be isolated from solution. There is good evidence, however, for the existence in solution of bromonium[2,3] and even chloronium[4] ions.

The previous work, on the mechanisms of basic[5] and thermal[6] decompositions of iodonium salts, is pertinent to the present polarographic reduction. Sandin and Brown's results[5] suggest that the decomposition of iodonium salts follows a free radical mechanism which is enhanced in the presence of some metals, for example mercury. Lucas, Kennedy and Wilmot[6] show that the decomposition under thermal conditions proceeds by scission of a C–I bond through an ionic mechanism. Medlin[7] has shown conclusively, by X-ray data, that the iodine–iodine bond in diphenyliodonium iodide is an ionic, not a covalent bond. Furthermore, the

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(1) K. Heller and E. N. Jenkins, *Nature*, **158**, 706 (1946).

(2) I. Roberts and G. E. Kimball, THIS JOURNAL, **59**, 947 (1937), interpreted P. D. Bartlett's and D. S. Tarbell's earlier kinetic studies in terms of a postulated intermediate bromonium ion.

(3) The extensive work of S. Winstein, H. J. Lucas and their co-workers proves conclusively that bromonium ions are real intermediates. See G. W. Wheland, "Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 242, and A. E. Remick, "Electronic Interpretations of Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 2nd Ed., 1949, p. 337, for a review of the subject.

(4) H. J. Lucas and C. W. Gould, THIS JOURNAL, **63**, 2541 (1941).

(5) R. B. Sandin and R. K. Brown, *ibid.*, **69**, 2253 (1947).

(6) H. J. Lucas, E. R. Kennedy and C. A. Wilmot, *ibid.*, **58**, 157 (1936).

(7) W. V. Medlin, *ibid.*, **57**, 1026 (1935).