4,4'-azobiphenyl was obtained from Professor H. Shine (Texas Technological College).

Acknowledgment. We are indebted to Mr. T. V. Atkinson and Dr. L. O. Wheeler for aid in the esr experiments, to Dr. K. S. V. Santhanam for helpful discussions during the course of the work, and to Professor H. Shine for a sample of 4,4'-azobiphenyl. The support of the Robert A. Welch Foundation and the National Science Foundation (GP 6688X) is gratefully acknowledged.

Electrochemical Reduction of Benzophenone in Aprotic Medium. Effect of Proton Availability

Ralph F. Michielli and Philip J. Elving

Contribution from the University of Michigan, Ann Arbor, Michigan.
Received September 27, 1967

Abstract: In aprotic medium (pyridine with tetraethylammonium perchlorate as background electrolyte), benzophenone is electrochemically reduced at a mercury electrode in two successive one-electron steps, first to the free radical anion and then to the benzhydrol dianion. Cyclic voltammetry indicates that the free radical is nearly reversibly reoxidized while the carbanion (or the pyridyl alcohol species resulting from its reaction with the solvent) and its monoprotonated form (formed by reaction with residual water in the solvent) are reoxidized with considerable overpotential compared to the second reduction step; a third cathodic wave at much less negative potential than the original two benzophenone reduction waves is due to reduction of the product arising from oxidation of the carbanion or derived pyridyl species. On addition of protons, additional mechanistic paths become operative; the second one-electron benzophenone reduction step merges with the first since the neutral free radical produced on the first electron transfer is more readily reduced than the anionic form (actually, it is reduced at the potential of initial reduction of benzophenone) and the anodic wave due to oxidation of the anionic free radical disappears. In addition, the anodic wave due to oxidation of the carbanion or pyridyl species decreases while that due to oxidation of the benzhydrol monoanion increases; this is accompanied by a decrease in the third cathodic wave with the growth of a fourth cathodic wave due to reduction of the free radical produced on oxidation of the benzhydrol monoanion.

The polarographic behavior of benzophenone has been extensively studied as a model for that of ketones in general. The mechanism and kinetics of the electrochemical reduction of benzophenone in aqueous and alcoholic-aqueous solution have been investigated, and the conditions for the formation of free radical and carbanion intermediates have been discussed.[1,2] In acidic and neutral media, two well-defined reduction waves, each corresponding to a one-electron process, are observed: the first wave is pH-dependent to the extent of *ca.* 60 mV/pH unit; the second is only slightly pH dependent. Above pH 6, the two waves merge into one pH-dependent wave whose height approximates the sum of the two waves in acidic media. At still higher pH, a third wave appears at more negative potential.

The following mechanism for reduction of benzophenone in aqueous solution is generally accepted. (1) In acidic media, the first one-electron wave represents the possibly reversible reduction of benzophenone to the free radical, $(C_6H_5)_2\dot{C}OH$, which can dimerize to pinacol; the second one-electron wave is due to reduction of the free radical to carbinol, which is assumed to be electrochemically irreversible. The pH dependence of the first wave is ascribed to the simultaneous polarization of the carbon–oxygen bond by the bonding of hydrogen ion to the oxygen as the ketone diffuses into the electrode field and as the electron is transferred to the molecule from the electrode. (2) The two-electron combined wave involves reduction of benzophenone to carbinol through the free-radical state. (3) Because of the relative proton scarcity in alkaline media, the free radical ion, $[(C_6H_5)_2\dot{C}O]^-$, is formed along with the neutral free radical; the third wave is attributed to the more difficult reduction of the free radical ion.

The most significant study of benzophenone reduction in nonaqueous media has been in dimethylformamide (DMF), where two waves are observed with the height of the second wave being 67 to 78% that of the first wave.[3,4] On addition of a "weak" acid, phenol, Given and Peover[3] found that wave I grew at the expense of wave II, which disappeared at an acid/ketone molar ratio of 2; addition of a stronger acid, benzoic acid, caused the appearance of a new wave at somewhat more positive potential, which grew at the expense of waves I and II (the latter disappeared at an acid/ketone ratio of 2). Wawzonek and Gundersen[4] observed that, on addition of water, wave I became slightly more positive and increased slightly in height, whereas wave II became much more positive and decreased appreciably in height.

In view of the importance of hydrogen ion or available proton in the electrochemical reduction of benzophenone, it was decided to investigate the behavior of benzophenone in an aprotic medium, namely pyridine, which is considered by Kolthoff[5] to be the

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(1) P. J. Elving and J. T. Leone, *J. Am. Chem. Soc.*, **80**, 1021 (1958).
(2) M. Suzuki and P. J. Elving, *J. Phys. Chem.*, **65**, 391 (1961).
(3) P. H. Given and M. E. Peover, *J. Chem. Soc.*, 385 (1960).
(4) S. Wawzonek and A. Gundersen, *J. Electrochem. Soc.*, **107**, 537 (1960).
(5) I. M. Kolthoff, *J. Polarog. Soc.*, **10**, 22 (1964).

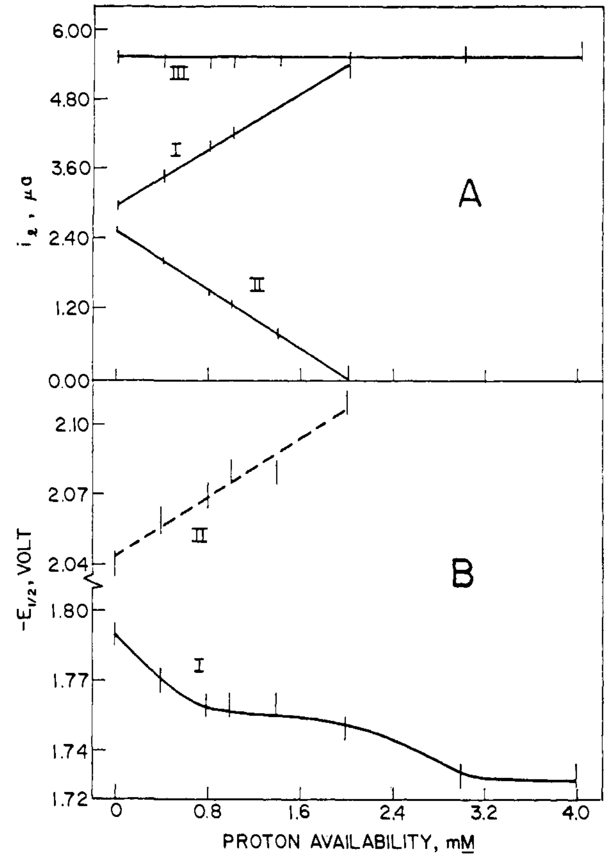

Figure 1. Variation of (A) limiting currents and (B) half-wave potentials of benzophenone waves on proton addition to 1.00 m*M* benzophenone in 0.1 *M* Et_4NClO_4 in pyridine: (I) first wave, (II) second wave, (III) sum of waves I and II. Potentials are plotted with a range of ±5 mV, the estimated error; currents are plotted with a 2% range.

only truly aprotic organic solvent; also studied was the extent of reversibility of the electrode processes in pyridine as indicated by cyclic voltammetric techniques. An earlier brief study of the polarographic behavior of benzophenone in pyridine solution revealed only a single one-electron reduction wave;[6] however, as subsequently discussed, the limited potential ranges available, due to decomposition of the supporting electrolytes used, prohibited observation of any wave(s) beyond the first one.

Proton availability in pyridine can be controlled by the addition of pyridinium salt (or a Brønsted acid which forms such a salt on dissolution in pyridine). Water, which is too weak an acid to be of much use as a proton source in DMF except when present in large concentration,[3,4] would be of even less effect in pyridine, although the possibility of it reacting with highly reactive anions cannot be *a priori* excluded.

Results and Discussion

Polarography at the Dme. Two well-defined polarographic waves ($E_{1/2} = -1.80$ and -2.03 V) are observed for benzophenone in pyridine (0.1 *M* Et_4NClO_4 as background electrolyte) (Table I; Figures 1 and 2). The current for each wave varies linearly with the square root of the mercury height and has a temperature coefficient of 1.1% deg^{-1}, indicating diffusion control. The diffusion-current constants of the waves show each to be due to a one-electron faradaic process.

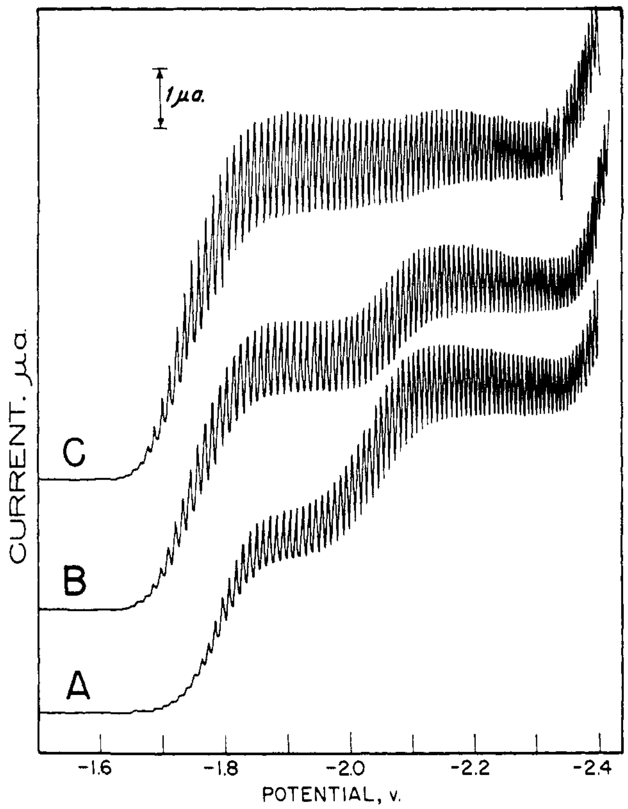

Figure 2. Polarograms of 1.00 m*M* benzophenone in 0.1 *M* Et_4NClO_4 in pyridine. Concentration of 3,4-dimethylphenol: (A) none, (B) 1.00 m*M*, (C) 2.00 m*M*.

Table I. Polarographic Behavior of Benzophenone in 0.1 *M* Et_4NClO_4–Pyridine[a]

Benzophenone concn, m*M*	Wave I			Wave II			Sum of waves	
	$-E_{1/2}$, V	i_1, μa	Slope,[b] mV	$-E_{1/2}$, V	i_1, μa	Slope,[b] mV	i_1/C	I[g]
0.51	1.79	1.64	59	2.01	1.40	66	5.96	4.35
0.51[c]	1.80	1.41	57	2.03	1.27	81	5.25	
0.51[d]	1.80	1.87	60	2.03	1.60	69	7.39	
0.51[e]	1.80	2.03	59	2.03	1.74	70	7.65	
1.00	1.79	2.96	58	2.04	2.54	72	5.50	4.01
1.00[f]	1.81	3.53	64	2.04	3.00	81	6.53	

[a] Data are reported for 25° and for $h = 41.0$ cm except where otherwise indicated. [b] Slope was calculated from $E_{1/4} - E_{3/4}$, which, for a reversible process, equals $56/n$ mV and, for an irreversible process, equals $56/\alpha n_a$ mV. [c] $h = 31.0$ cm. [d] $h = 51.1$ cm. [e] $h = 61.7$ cm. [f] Temperature 40°. [g] Diffusion current constant, $I = i_1/Cm^{2/3}t^{1/6}$.

Since Cizak and Elving[6] reported only one one-electron reversible wave for benzophene at the dme in pyridine containing 0.1 *M* LiCl, 1.0 *M* $LiNO_3$, or 0.15 *M* Bu_4NI as background electrolyte, a pyridine solution of benzophenone, which was 0.1 *M* in $LiClO_4$, was examined; one wave ($E_{1/2} = -1.56$ V; $I = 2.11$; slope = 45 mV) was observed, which would correspond to the first wave observed in 0.1 *M* Et_4NClO_4 ($E_{1/2} = -1.80$ V; $I = 2.26$; slope = 59 mV). The second wave seen in Et_4NClO_4 solution is not observed

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(6) A. Cizak and P. J. Elving, *Rev. Polarogr.* (Kyoto), **11**, 21 (1963).

in the other background electrolytes mentioned because of the more limited potential ranges of these electrolytes compared to that of Et_4NClO_4. However, the beginning of a second wave, obscured by background discharge, was observed in $LiClO_4$ solution. The decomposition potentials of 0.1 *M* solutions of Et_4NClO_4 and $LiClO_4$ are −2.4 and −2.0 V, respectively;[7] decomposition potentials of the electrolytes used by Cizak and Elving[6] are less than that of $LiClO_4$. Consequently, the one wave reported by the latter is actually the first of the two waves observed in pyridine solution of sufficiently stable background electrolyte.

Effect of Proton Addition. The appearance of two one-electron waves for the over-all two-electron reduction of the benzophenone carbonyl bond in pyridine solution is typical of the reduction of double-bond systems in proton-poor media; since the two one-electron processes generally coalesce in proton-available media to give a single two-electron wave,[8,9] the effect of proton addition to a benzophenone solution in pyridine was investigated.

When a Brønsted acid is dissolved in pyridine, the acidic protons combine with pyridine molecules to form pyridinium ions. Polarographic reduction of pyridinium ion in pyridine solution involves reduction of the pyridine ring;[10,11] in pyridine containing 0.1 *M* Et_4NClO_4 as supporting electrolyte, $E_{1/2}$ for the pyridinium ion reduction varies with the nature and aqueous pK_a of the acid.[7,12] For the present study, 3,4-dimethylphenol was chosen as the proton source because its $E_{1/2}$ is more negative than those of the benzophenone waves.[12]

Addition of a proton source caused the first benzophenone wave to grow at the expense of the second wave (Table II; Figures 1 and 2) until only a single wave was left at a 2:1 ratio of proton to benzophenone. Further addition of protons up to a 4:1 ratio does not significantly change the height of the first wave, which now represents the two-electron reduction of benzophenone; the second wave seen is due to the reduction of pyridinium ion, which reaches the electrode without reversion to pyridine because of consumption of its hydrogen ion in the benzophenone reduction.

Table II. Effect of Proton Addition to 1.0 m*M* Benzophenone in 0.1 *M* Et_4NClO_4–Pyridine at 25°

DMP[a]	Wave I			Wave II			Total	
concn, m*M*	$-E_{1/2}$, V	i_l, μa	Slope,[b] mV	$-E_{1/2}$, V	i_l, μa	Slope,[b] mV	i_l, μa	i_{II}/i_I
0	1.79	2.96	58	2.04	2.54	72	5.50	0.86
0.4	1.77	3.47	79	2.06	2.00	65	5.47	0.58
0.8	1.76	3.97	78	2.07	1.48	63	5.45	0.37
1.0	1.76	4.21	78	2.08	1.26	57	5.47	0.30
1.4	1.76	4.72	78	2.08	0.75	47	5.47	0.16
2.0	1.75	5.25	77	2.11	0.28	...[c]	5.53	0.05
3.0	1.73	5.60	66	(2.15	1.73	70)[d]		
4.0	1.73	5.70	72	(2.14	3.83	85)[d]		
2.0[e]				(2.08	4.65	124)[d]		

[a] DMP = 3,4-dimethylphenol. [b] Slope calculated from $E_{1/4} - E_{3/4}$. [c] Slope could not be obtained because wave was too small. [d] Wave due to reduction of pyridinium ion. [e] No benzophenone present.

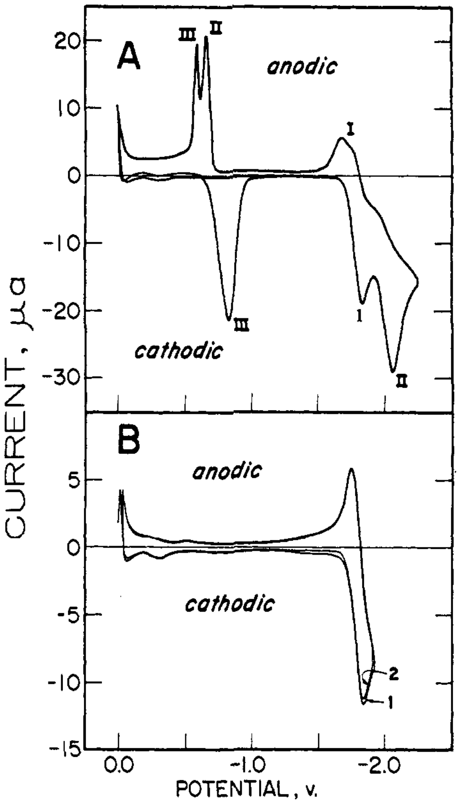

Figure 3. Cyclic voltammograms at the hmde of 1.0 m*M* benzophenone in 0.1 *M* Et_4NClO_4 in pyridine (scan rate, 200 mV/sec). (A) Potential span including all waves. (B) Potential span restricted to that of the first waves. Roman numbers refer to waves (*cf.* text); arabic numbers to number of scan.

The presence of a very small benzophenone wave II (*ca.* 5% of the total current) in a solution of 2.0 m*M* 3,4-dimethylphenol and 1.0 m*M* benzophenone is presumably due to a small deficiency of acid, since the purity of the acid was not known with certainty (being a phenol, it is not easily kept dry); this is confirmed by the magnitude of wave I in the presence of excess proton source and by calculations based on the pyridinium ion reduction wave (the latter is a long drawn-out wave as indicated by its slope). The possibility that small wave II at a 2:1 proton:benzophenone ratio is due to equilibrium effects is not inconsistent with the data, although not likely. It is possible that a difference in diffusion rates of benzophenone and pyridinium ion or ion-pair formation in pyridine might account for the phenomenon.

Cyclic Voltammetry at the Hmde. On the first scan, cyclic voltammograms of benzophenone in pyridine show two cathodic and three anodic waves; on succeeding scans, a third cathodic wave appears at a potential more positive than those of the first two waves (Figure 3A) (Roman numerals will be used to designate the wave and letters "a" and "c" to designate "anodic" and "cathodic," respectively). The technique of wave clipping established that the first anodic wave, Ia, is caused by reoxidation of the species produced in the

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(7) J. E. Hickey, M. S. Spritzer, and P. J. Elving, *Anal. Chim. Acta*, **35**, 277 (1966).

(8) P. G. Grodzka and P. J. Elving, *J. Electrochem. Soc.*, **110**, 225 (1963).

(9) P. G. Grodzka and P. J. Elving, *ibid.*, **110**, 231 (1963).

(10) M. S. Spritzer, J. M. Costa, and P. J. Elving, *Anal. Chem.*, **37**, 211 (1965).

(11) A. Cizak and P. J. Elving, *Electrochim. Acta*, **10**, 935 (1965).

(12) K. Tsuji and P. J. Elving, work in progress.

first cathodic step, Ic; *e.g.*, scanning in a negative direction from 0.00 V to some potential (switching potential) between cathodic waves I and II, such as −1.95 V, and then back again in a positive direction to 0.00 V, gives a voltammogram which shows only cathodic wave I and anodic wave I (Figure 3B).

Waves IIa and IIIa result from the oxidation of the species formed in the second reduction step, wave IIc. IIa is well defined, but IIIa occurs on the decaying portion of the current for IIa and is not always reproducible.

Wave clipping established that wave IIIc, which appears on the second and succeeding scans, results from the reduction of the species formed in step IIa.

Addition of protons to the test solution results in informative changes in the voltammetric pattern. With increasing proton availability, wave Ic grows at the expense of IIc, as is also observed polarographically. Concurrently, wave Ia becomes smaller and disappears at a proton:benzophenone ratio of 2:1. Simultaneously, wave IIIa shifts to more positive potential and grows at the expense of IIa until the latter is eliminated at a proton:benzophenone ratio slightly below 0.8:1.0. As wave IIIa shifts on proton addition, wave IIIc splits, producing a new cathodic wave, IVc, at a less negative potential; wave IVc grows with increasing proton availability at the expense of IIIc until the latter is eliminated at a proton:benzophenone ratio slightly above 1.4:1.0.

Only wave IVc at the slower scan rate shows an appreciable shift in potential on proton addition up to a ratio of two protons per benzophenone, *i.e.*, from −0.50 to −0.35 V. All other waves vary by less than 0.05 V in peak potential except for wave IIIa, which is at −0.60 in the absence of added proton and which varies from −0.35 to −0.30 between 0.4 and 2.0 m*M* phenol.

Benzhydrol and Benzpinacol. A 1 m*M* solution of benzhydrol in pyridine (0.1 *M* Et_4NClO_4) showed no waves on polarography at the dme or on cyclic voltammetry at the hmde.

A similar benzpinacol solution showed only the patterns characteristic of benzophenone itself, evidently due to the decomposition of benzpinacol under alkaline conditions.[13]

Electrode Reaction Mechanism

Reversibility. At the dme, the slopes of waves Ic and IIc are 59 and 72 mV, respectively, as calculated from $E_{1/4} - E_{3/4}$ data (the theoretical slope for a reversible one-electron process at 25° is 56 mV).

For an electrochemically reversible couple at a stationary electrode at 25°, theory[14,15] predicts that, for a one-electron process, $E_p = E_{1/2} - 0.028$, $E_{p/2} = E_{1/2} + 0.028$ V, and $E_p = E_{p/2} - 0.056$ V for a cathodic reaction, and $E_p = E_{1/2} + 0.028$, $E_{p/2} = E_{1/2} - 0.028$, and $E_p = E_{p/2} + 0.056$ V for an anodic reaction with ΔE_p (anodic–cathodic), $\Delta E_{p/2}$ (cathodic–anodic), and $\Delta(E_p - E_{p/2})$ then being 0.056 V. For benzophenone in pyridine (Table III), $\Delta E_p = 0.090$ V, $\Delta E_{p/2} = 0.030$ V, and $\Delta(E_p - E_{p/2}) = 0.07$ (cathodic) and 0.05 V (anodic) for reduction wave I; $E_{p/2}$ values show only a small variation from $E_{1/2}$ for both Ic and IIc (Table II). Unfortunately, the cyclic voltammetric data permitted valid calculation of potentials only to two decimal places. With this in mind, it can be safely asserted that both the data and the appearance of the voltammogram indicate at least a quasi-reversible couple for the process producing wave I. For reduction wave II, $\Delta E_p = 1.43$ V and $\Delta E_{p/2} = 1.35$ V, indicating an over-all electrochemically irreversible couple; however, $\Delta(E_p - E_{p/2}) = 0.06 \pm 0.01$ (cathodic) and 0.03 V (anodic), which may indicate reversibility in the controlling step for the second reduction wave.

Table III. Cyclic Voltammetry of Benzophenone in 0.1 *M* Et_4NClO_4–Pyridine at the Hmde at 25°

Sweep rate, mV/sec		Cathodic waves			Anodic waves[a]		
		$-E_p$, V	$-E_{p/2}$, V	i_p, μa	$-E_p$, V	$-E_{p/2}$, V	i_p, μa
		0.51 m*M* Benzophenone					
200	I	1.84	1.77	12.5	1.75	1.80	2.8
	II	2.11	2.06	9.6	0.68	0.71	7.0
200	I	1.84	1.77	12.5	1.75	1.80	6.8
	II[b]						
40	I	1.84	1.77	6.8	1.74	1.78	2.6
	II	2.08	2.02	5.0	*c*	*c*	*c*
		1.0 m*M* Benzophenone					
200	I	1.84	1.77	20.5	1.75	1.80	5.0
	II	2.12	2.05	16.5	*c*	*c*	*c*
200	I	1.84	1.77	20.8	1.75	1.80	10.0
	II[b]						
40	I	1.84	1.77	10.0	1.75	1.80	2.5
	II	2.08	2.03	9.0	*c*	*c*	*c*

[a] E_p for anodic wave III = −0.55 V at a sweep rate of 200 mV/sec. Other data are not available because the wave is not well defined; *cf.* text. [b] The switching potential was too positive to allow wave II to be seen. [c] The starting potential was too negative to allow sweeping back to wave II.

Effect of Proton Addition. While the limiting current for benzophenone wave Ic increases linearly with proton addition at the expense of that for wave IIc, the $E_{1/2}$ values seem to behave oddly (Figure 1); while $E_{1/2}$ for wave I becomes more positive with increasing proton population as would be expected for proton participation in the energy-controlling step of the electrode reaction, $E_{1/2}$ for wave II becomes more negative with increasing proton population.

Careful examination of the polarographic curves, *e.g.*, Figure 2, reveals the phenomenological basis for the contrary variation of $E_{1/2}$. As the proton population is increased, wave I starts at more and more positive potential as is demanded by its growth in size as well as by a shift to more positive potential due to $E_{1/2}$ shift; however, it seems to end at about the same potential in all cases. Under the same conditions, wave II, which is growing smaller, starts at less positive potential, as expected for a decreasing height, but ends at essentially the same potential in all cases. The result of such behavior is that the measured $E_{1/2}$ for wave I becomes less negative but its slope becomes less with increasing proton availability, whereas the measured $E_{1/2}$ for wave II becomes more negative but its slope becomes greater (*cf.* Table II, where an increase in millivolts for the slope denotes a less steep slope).

The behavior of the waves on proton addition, just described, can be rationalized on the basis that wave I

(13) W. Kemula, Z. R. Grabowski, and M. K. Kalinowski, *Collection Czech. Chem. Commun.*, 25, 3306 (1960).

(14) L. Meites, "Polarographic Techniques," Interscience Publishers, Inc., New York, N. Y., 1965, Chapter 8.

(15) P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954, Chapter 6.

involves two electron-transfer processes, as protons are added up to a molar proton:benzophenone ratio of 2: a proton-assisted process, which is facilitated in respect to potential required and is increased in magnitude by increasing proton population, plus a proton-independent process. The constancy of the peak potential of waves Ic and IIc would then be due to the predominance of the pH-independent processes under conditions of rapid polarization.

Because of the lack of knowledge of actual proton activity in solutions of pyridinium salts in pyridine, calculations of the variation of potential with proton availability must be made with caution. However, it is clear that the two-electron reduction of benzophenone consumes two protons (current behavior in Table III).

Electrode Processes. Cathodic Waves I and II. The available data indicate that the rates of intervening chemical reactions do not control to any significant extent the observed potentials; accordingly, any chemical reactions that are involved, *e.g.*, proton acquisition, must be rapid in comparison with the electron-transfer processes which occur.

Consequently, a mechanism is suggested for the reduction of benzophenone in pyridine solution whereby benzophenone, in the absence of protons, is first reduced to an anion free radical (II) in a one-electron reversible step; in a second one-electron step, which may be reversible, the free radical is reduced to a carbanion (III) with the final product being a salt of the benzhydrol anion or a pyridyl alcohol species resulting from attack on the solvent (*cf.* subsequent discussion). The slightly lower value for the limiting current of wave II *vs.* that of wave I (Table I; *ca.* 15%) may be due to one or more of the following: (a) repulsion of the ketyl anion from the electrode; (b) dimerization to a product which is nonreducible in the potential range available; (c) formation during the wave I process of the $(C_6H_5)_2\dot{C}OH$ free radical (from II and any water which may be present in the solvent), which is reducible at the wave I potential as formed; (d) disproportionation of the ketyl anion to benzophenone and the dianion

$$\underset{\text{I}}{(C_6H_5)_2C{=}O} + e \longrightarrow \underset{\text{II}}{[(C_6H_5)_2\dot{C}{-}O]^-} \qquad (1)$$

$$\text{II} + e \longrightarrow \underset{\text{III}}{[(C_6H_5)_2\ddot{C}{-}O]^{2-}} \qquad (2)$$

$$2\text{II} \longrightarrow \text{I} + \text{III} \qquad (3)$$

However, reaction 3 is considered not to be energetically feasible.[16]

Explanation c is most reasonable in view of the constancy of the total current on proton addition (Table II).

In the presence of protons, the reduction of benzophenone to benzhydrol can also occur by a mechanism of the type proposed by Hoijtink, *et al.*,[17] for the reduction of double bonds in solvents which are poor proton donors.

$$\text{I} + e \longrightarrow \text{II} \qquad (4)$$

$$\text{II} + \text{pyH}^+ \longrightarrow \underset{\text{IV}}{(C_6H_5)_2\dot{C}{-}OH} + \text{py} \qquad (5)$$

$$\text{IV} + e \longrightarrow \underset{\text{V}}{[(C_6H_5)_2\ddot{C}{-}OH]^-} \qquad (6)$$

$$\text{V} + \text{pyH}^+ \longrightarrow \underset{\text{VI}}{(C_6H_5)_2CHOH} + \text{py} \qquad (7)$$

The rate of proton addition to the free radical anion II is assumed to be faster than its rate of diffusion away from the electrode surface so that free radical IV is formed in the electrode layer. Reactions 4 and 5 probably involve a transition state or species in which, as an electron is transferred to the carbonyl carbon, a proton is simultaneously bonded to the carbonyl oxygen,[1] as indicated by the easier reduction with increasing proton availability. Since free radical IV is more easily reduced than benzophenone,[18] one would expect the height of the first wave to increase at the expense of that of the second wave with increasing proton concentration, as is observed. The one benzophenone wave observed at a proton:benzophenone ratio of 2:1 or greater involves the over-all addition of two electrons.

The polarographic behavior of benzophenone in pyridine as the proton donor concentration is increased shows type A behavior as classified by Given and Peover;[3] *i.e.*, wave I grows at the expense of wave II until the latter disappears. It is assumed in reaction 5 that the undissociated acid rather than the solvated proton is involved in protonation of the ketyl radical, but it is not certain which form is involved. However, the equation for the single wave representing a two-electron addition has been derived[3] for the case where a sufficient excess of proton donor is present to ensure that the two waves coalesce completely and where the proton donor is the undissociated acid; the potential of the dme is then given by

$$E_{\text{dme}} = \text{constant} + \frac{RT}{F}\ln\frac{(i_d - i)(mi_d/2 - i)}{i} \qquad (8)$$

$$E_{1/2} = \text{constant} + \frac{RT}{F}\ln\frac{i_d}{2} + \frac{RT}{F}\ln(m - 1) \qquad (9)$$

where m is the ratio of molar proton donor concentration to ketone concentration and the other symbols have their usual significance.

A plot of E_{dme} *vs.* the logarithmic term in eq 8, which results in a straight line, would indicate that the undissociated acid rather than the solvated proton is the effective proton donor.

Plots of E_{dme} *vs.* $\log[(i_d - i)(mi_d/2 - i)/i]$ for $m = 3.0$ and of E_{dme} *vs.* $\log[(i_d - i)/i]$ (Figure 4) both show a tendency for curvature toward the top of the wave and, thus, while favoring the view that the undissociated acid is involved in the protonation of the ketyl radical, are not entirely conclusive.

The half-wave potentials vary with m in the required direction but by slightly less than the magnitude required by eq 9, *i.e.*, $\Delta E_{1/2} = 20$ mV experimentally *vs.* 28 mV calculated theoretically. The magnitude of the discrepancy is of the same order as that observed for benzophenone–phenol in DMF.[3]

Anodic Waves. Anodic wave Ia, observed on cyclic voltammetry, represents reoxidation of the original free radical, *i.e.*, the reverse of eq 1. The reversibility of the process may be due to the symmetrical nature of the free radical compared to the original species; the electron-transfer process is unaccompanied by the breaking

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[16] N. S. Hush and J. Blackledge, *J. Chem. Phys.*, 23, 514 (1955).

[17] G. J. Hoijtink, J. van Schooten, E. de Boer, and W. Y. Aalbersberg, *Rec. Trav. Chim.*, 37, 355 (1954).

[18] C. L. Perrin, *Progr. Phys. Org. Chem.*, 3, 222 (1965).

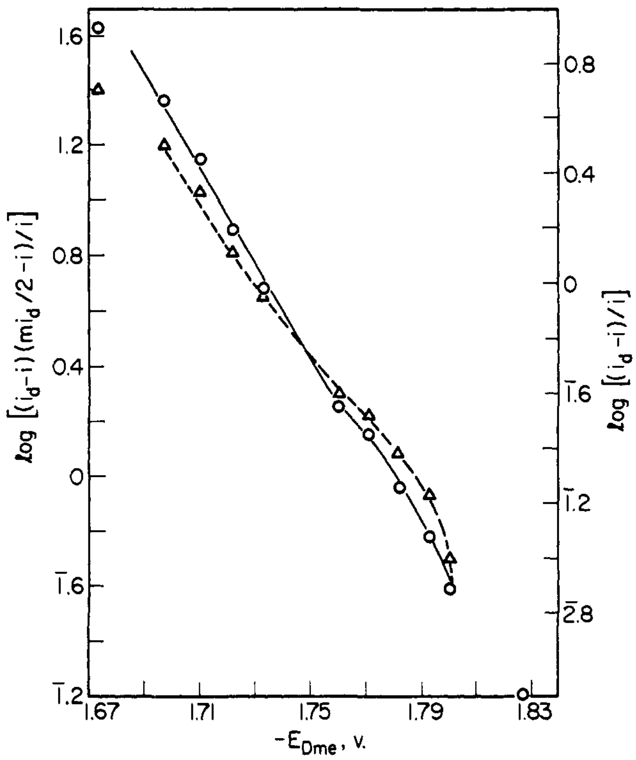

Figure 4. Logarithmic analysis of wave of 1.0 mM benzophenone in 0.1 M Et_4NClO_4 and 3 mM 3,4-dimethylphenol in pyridine (situation where molar ratio m = 3): (solid line) E_{dme} *vs.* log $[(i_d - i)\cdot(mi_d/2 - i)/i]$; (dashed line) E_{dme} *vs.* log $[(i_d - i)/i]$.

or re-forming of bonds which might introduce additional energy-controlling factors.

Waves IIa and IIIa are most likely due to the oxidation of species such as $[(C_6H_5)_2\ddot{C}\text{-}O]^{2-}$, $(C_6H_5)_2CH\text{-}O^-$, or $(C_6H_5)_2CHOH$; involvement of any pinacol species is excluded by the nonappearance of waves IIa and IIIa upon wave clipping after wave Ic. Benzhydrol in pyridine solution showed no electrochemical reactivity at the mercury electrode. Wave IIa, then, is due to reoxidation of the original carbanion, *i.e.*, the reverse of eq 2 and 1, or, more likely, the oxidation of a pyridyl alcohol species resulting from attack of the carbanion on the solvent (*cf.* subsequent discussion), while wave IIIa is due to oxidation of a protonated carbanion; this is in accord with the experimentally observed growth of wave IIIa at the expense of wave IIa and its shift to more positive potential as available proton is added to the solution.

The elimination of wave IIa at a proton:benzophenone concentration of slightly less than 1:1 indicates that the carbanion need be only monoprotonated for wave IIIa to be produced; the initial small size and nonreproducibility of wave IIIa in absence of added available proton would then be due to formation of a minute amount of monoprotonated carbanion by interaction of the dianion with the low proton activity arising from the trace of water in the solvent.

Cathodic Waves III and IV. Bachman, *et al.*,[19] showed that the reduction of carbonyl compounds with various metals in pyridine solution results in the formation of pyridyl alcohols; since pyridine is readily attacked by anions, preferentially at the 2 and 4 positions, and is slowly attacked by free radicals,[20] the postulated reaction mechanism involved reduction of the carbonyl bond by a two-electron process to a carbanion, which would attack the pyridine to form a pyridyl alcohol. Interaction of the carbanion produced in the electrochemical reduction of benzophenone (eq 2) with solvent pyridine could result in formation of a pyridyl alcohol or a similar species, X, which forms the oxidation-reduction couple X, Z

$$X \underset{\text{IIIc}}{\overset{\text{IIa}}{\rightleftarrows}} Z + ne \tag{10}$$

where IIa and IIIc refer to the oxidation and reduction waves, respectively.

Since the presence of protons would hamper the formation of the carbanion or would neutralize it, increasing the proton availability should result in a smaller amount of X being formed, with consequent decreases in the heights of waves IIa and IIIc; this is observed experimentally.

If, as postulated, wave IIIa is due to the oxidation of the monoanion resulting from protonation of the carbanion found in process IIc, *i.e.*, benzhydrol anion, and if wave IVc is due to reduction of the free radical formed in process IIIa, *i.e.*

$$(C_6H_5)_2CH\text{—}O^- \underset{\text{IVc}}{\overset{\text{IIIa}}{\rightleftarrows}} (C_6H_5)_2CH\text{—}O + e \tag{11}$$

one would expect both waves IIIa and IVc to grow with increasing proton availability, as is indeed observed experimentally.

Reputed Benzpinacol Oxidation. Cyclic voltammetry at the hmde of benzophenone in alkaline aqueous ethanol solution has been reported to result in voltammograms with one cathodic wave and two anodic waves.[21] The two anodic waves, which are separated by *ca.* 1.1 V, are attributed to oxidation of (a) ketyl radicals formed in the ketone reduction and (b) benzpinacol formed by dimerization of ketyl radicals and subsequent hydrolysis. Since, in pyridine solution, the separation of waves Ia and IIa is *ca.* 1.1 V and the possibility of pinacol species as being responsible for wave IIa has been excluded, it seems likely that the oxidation waves observed by Kemula, *et al.*,[21] correspond to waves Ia and IIa in pyridine.

Kemula, *et al.*,[13] also reported the oxidation of benzpinacol to benzophenone at the dme in alkaline aqueous ethanol solution. Attempts at duplication of the experiments in aqueous solution under conditions as identical as possible with those used by Kemula, *et al.*, were unsuccessful, as were also attempts at oxidation of benzpinacol in pyridine solution; only the reduction waves of benzophenone, produced in the chemical decomposition of the pinacol, were observed.

Experimental Section

Chemicals. Benzophenone, benzhydrol, and 3,4-dimethylphenol (Eastman, White Label) and benzpinacol (Columbia Organic Chemicals) were used as received. Lithium perchlorate (G. F. Smith Chemical Co., anhydrous reagent) was dried at 130°. Tetraethylammonium perchlorate (Eastman, White Label) was vacuum dried at room temperature for 24 hr. Pyridine (J. T. Baker, rea-

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[20] R. C. Elderfield, "Heterocyclic Compounds," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1950.

[21] W. Kemula, Z. R. Grabowski, and M. K. Kalinowski, *Naturwissenschaften*, 47, 514 (1960).

gent) was purified by fractional crystallization.[22] Argon, used for deoxygenating test solutions, was passed through a column of Drierite and then through pyridine thermostated at the same temperature as that of the test solution. Triple-distilled mercury was used for the dropping mercury electrode (dme).

Apparatus. Polarograms were recorded with a Leeds and Northrup Electro-Chemograph Type E, used in conjunction with an IR compensator.[23]

Cyclic voltammograms, obtained with an operational amplifier control circuit,[24] were recorded on Moseley Model 135 and 7035A X–Y recorders. The hanging mercury drop electrode (hmde), used as the indicating electrode, consisted of a platinum wire sealed in the end of a piece of glass tubing, filed flush with the end of the tubing and then plated with mercury.

Capillary constants of the dme at a mercury height of 41.0 cm (uncorrected for back pressure) in deoxygenated 0.1 M Et_4NClO_4 in pyridine solution at 25° and at open circuit were $m = 1.24$ mg/sec and $t = 5.70$ sec; $m^{2/3}t^{1/6} = 1.54$.

The jacketed three-compartment cell used has been described.[7] The temperature was regulated to 25 ± 0.2° except where indicated otherwise.

Potentials were measured *vs.* the $Ag|AgNO_3$ (1 M in pyridine) electrode, NAgE,[25] whose potential is +0.09 V *vs.* the aqueous saturated calomel electrode (liquid junction potentials included).

Procedures. Stock solutions of background electrolytes were prepared by dissolving weighed quantities and diluting to known volume. Stock solutions of benzophenone and 3,4-dimethylphenol were prepared by dissolving weighed quantities in and diluting to known volume with stock background solution. Tests solutions were prepared by pipetting appropriate amounts of stock solutions into 10-ml volumetric flasks and diluting to volume with background solution.

Argon was bubbled through the test solution for 10 min. The dme was then inserted and polarograms were recorded with argon passing over the solution.

For cyclic runs at the hmde, two drops of mercury were collected from the dme capillary, which was inserted in the test solution, and were hung on the hanging drop electrode assembly. Potentials were scanned in a negative direction to some preset potential and then back to the starting potential. Scan rates were 40 and 200 mV/sec.

Acknowledgment. The authors thank the Petroleum Research Fund of the American Chemical Society and the National Science Foundation, which helped support the work described.

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Organometallic Electrochemistry. XI.[1] Stable Radical Anions Derived from Acetylene–Metal Carbonyl Complexes

Raymond E. Dessy and Rudolph L. Pohl

Contribution from the Department of Chemistry, Virginia Polytechnic Institute, Blacksburg, Virginia.

Received July 19, 1967

Abstract: The electrochemical behavior of 35 metal–acetylene complexes have been explored. Evidence for stable anion radical and dianion formation has been found in many cases. Dianion production may result from two one-electron steps, or by one two-electron step. Several examples in which structural reorganization of the molecule occurs upon reduction are reported.

Two previous papers in this series have demonstrated that cyclic polyolefin π complexes of $Fe(CO)_3$ such as $(\pi\text{-}C_8H_8)Fe(CO)_3$ and $(\pi\text{-}C_6H_8)Fe(CO)_3$ are capable of yielding, upon reduction, stable radical anions. During the past decade a number of complexes derived from reactions of various acetylenes with one of the three iron carbonyl parent materials, $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$, have been reported. These contain a variety of π-complexed organic fragments ranging from cyclobutadiene derivatives to substituted tropones.

It has recently been found in our laboratory that in many cases these compounds reduce to give quite stable radical anions and dianions. The presence in the same molecule (both neutral parent and radical anion and dianion reduction products) of coordinated CO ligands, π-complexed organic unsaturated ring systems, and iron atoms permits the use of infrared spectroscopy, electron spin resonance spectroscopy, and Mössbauer spectroscopy to evaluate the location of unpaired electron density and symmetry in the radical anion. This paper reports on the new radical anion and dianions prepared for this study and presents their electrochemical and electron spin resonance characteristics. Experimental work in the remaining two areas is extremely slow and will be reported in a subsequent publication.

Preliminary concepts, derived from the work of Gray,[2] Holm,[3] and Dahl[4] and unpublished work from this laboratory,[5,6] suggest that, when a coordination complex of a transition metal is reduced (or oxidized), the locus of high-spin density in the radical anion (or cation) may range between two extremes. The first is occupation of an orbital which is predominantly metal in origin, giving rise to unusual oxidation states of the metal. The second is occupation of an orbital which is predominantly ligand in character, giving rise to a ligand radical anion (or cation) stabilized by coordina-

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[1] For previous papers in this series see R. E. Dessy, *et al.*, *J. Am. Chem. Soc.*, **88**, 453, 460, 467, 471, 5112, 5117, 5121, 5124, 5129, 5132 (1966).

[2] H. B. Gray, personal communication.

[3] R. Holm, personal communication.

[4] L. Dahl, personal communication.

[5] Gordon Conference on Electrochemistry, Santa Barbara, Calif., Jan 1967.

[6] The first suggestions along these lines appear to have been proferred in a personal communication of Professor Larry Dahl to one of the present authors (R. E. D.) in Sept 1965.